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Optimisation of Co-Firing of High Moisture Biomass with Coal in a Bubbling Fluidised Bed Combustor

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A Thesis submitted in Partial Fulfillment of the requirements ofthe Degree of Doctor of Philosophy in the Faculty of Advanced Technology, University of Glamorgan

R11

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بسم الله الرحمن الرحيم

In the name of Allah, the Most Gracious, the Most Merciful

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Publications

- J. Ward, M. Akram and R. Garwood, (2011), "Co-Firing of Coal and Pressed Sugar Beet Pulp in a PilotScale Fluidised Bed Combustor", 9th European Conference on Industrial Furnaces and Boilers (INFUB), 26th – 29th of Aril, 2011, Estoril, Portugal.

- J. Ward, M. Akram and R. Garwood, (2011), "Fluidised Bed Combustion of Blends of Coal and Pressed sugar Beet Pulp", 8th Thermal Engineering Joint Conference (AJTEC2011), March 13 – 17, 2011, Honolulu, Hawaii, USA.

Abstract

The work presented in this thesis was carried out with a particular view of enhancing the capacity of coal fired fluidised bed hot gas generator (HGG) at the Cantley factory of British Sugar. It covers combustion of coal and biomass and their blends also called co-firing in a fluidised bed combustor. Particularly it focuses on the effect of introduction of moisture as part of fuel or injection of water into the bed on the reduction of excess air to get a stable bed temperature. Although this thesis is focused on increasing the throughput of the HGG, the study has a broad application and can be beneficial in utilising relatively cheap, poor quality, unprepared biomass materials. The results of this study can be helpful in devising systems to deal with wastes from different industries in co-combustion with a fuel of higher calorific value such as coal. Thus the study will have dual impact on the industry; addressing waste management issues on one hand and producing useful energy on the other. This may contribute towards meeting the targets of Kyoto Protocol by reducing emissions of carbon dioxide (CO_2) as biomass is thought to be CO_2 neutral.

The fluidised bed at Cantley is used to dry animal feed and has a design capacity of 40 MW but due to limitations of flow of fluidising gases caused by high flow resistance through sparge pipes, the combustor is running under capacity. Consequently, some of the animal feed has to be dried by using expensive oil fired drier.

In any combustion system excess air is used to control combustion temperature. In fluidised bed combustion excess air is used to control bed temperature. If the bed is cooled by other means the requirement of excess air can be reduced. This is the basic idea behind this study which is aimed at enhancing the capacity of the HGG by cooling the bed and thus reducing excess air requirements. The excess air thus spared can be used to combust more coal in the bed and thus will reduce dependence on oil fired dryer and will have financial benefits for British Sugar.

Different fuels including wood pellets, wood chips and sugar industry by-products such as vinasse, raffinate and pressed pulp were fired/cofired with Thoresby coal in a fluidised bed test rig installed at the University of Glamorgan. The blends of wood chips and pressed pulp

with coal are co-fired at different moisture contents. The tests were conducted at different thermal inputs at a wide range of excess air levels.

Most of the work is focusedon the combustion of blends of coal and pressed pulp in different proportions. It was found that the maximum proportion of the pressed pulp in the blend with coal which could be burned successfully in the fluidised bed is 50%. During combustion of different coal-pulp and coal-wood chips blends it was found that excess air requirement is reduced by around 20% in comparison to coal only firing, over the range of the operating conditions tested.

Because of the presence of potassium in pressed pulp, which could cause agglomeration during combustion in fluidised beds, longer term tests were carried out with 50/50 blend of coal and pulp. No signs of agglomeration were observed when the rig was fired for 8 days for almost 7 hours a day. However, Scanning Electron Microscopy (SEM) analyses of bed samples taken at the end of every day have shown the accumulation of potassium in the bed up to 1%. For comparison purposes tests were also carried out by co-firing coal with raffiante and vinasse and then it was observed that the bed defluidised relatively quickly, within 40 minutes of co-firing. Post experiment SEM analysis confirmed the accumulation of potassium in the bed which was found to be around 8% for raffinate and around 10% for the vinasse experiment.

It was found that the pulp is difficult to deal with and particularly its feeding into the fluidised bed could be a potential problem. Therefore, injection of water into the bed, a relatively cheaper and adaptable option, was also investigated. It was found that emissions of carbon monoxide due to incomplete combustion or water gas shift reaction would not be a problem as long as the bed temperature is controlled above 800 °C. It was found that the injection of water at a rate of 4.5 l/h into the bed fired at 17 kW reduced the air flow requirement by around 7.5 m^3/h which corresponds to a reduction of almost 20% which agrees with the finding with coal-pulp blends co-firing.This excess air can be used to burn around 5 kW equivalent of more coaland thus result in an increase in the thermal capacity by around 30%. Therefore, it may be possible to enhance the thermal capacity of the HGG at Cantley by 30% by injecting water into the bed or by co-firing coal and pulp.

Table of Contents

List of Figures

List of Tables

Acronymes and Abbreviations

°C	Degree Centigrade
°C/s	Degree Centigrade per second
15%M	Blend of 15% moisture content wood chips with coal (50/50, wt/wt)
55%M	Blend of 55% moisture content wood chips with coal (50/50, wt/wt)
A	Alkali index A
A/F	Air to Fuel ratio
AI	Agglomeration Indicator
Al	Aluminium
$Al(OH)_3$	Gibbsite
Al_2O_3	Aluminium oxide
$Al_4Si_4O_{10}(OH)_8$	Kaolin
AOGCMs	Atmospheric – Ocean General Circulation Models
APAS	Activite de Promotion, D'Accompagnement et de Suivi
AR	As Received
ASTM	American Standard for Testing Materials
B.O.D	Biological Oxygen Demand
bara	Bar atmospheric (pressure)
barg	Bar gauge (pressure)
BCURA	British Coal Utilisation Research Association
BFB	Bubbling Fluidised Bed
BP	Bed Pressure
Brix	Degrees Brix (symbol °Bx) is the sugar content of an aqueous solution
BS	British Standard
BT	Bed Temperature (°C)
BTU	British Thermal Unit

C	Carbon
Ca	Calcium
$Ca(OH)_2$	Calcuim hydroxide
$Ca_2P_2O_7$	Calcium Pyrophosphate
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcium Carbonate
CaO	Calcium oxide
$CaSiO_3$	Calcium Silicate
$CaSO_4$	Calcium sulphate
CFB	Circulating Fluidised Bed
CFD	Computational Fluid Dynamics
CH_4	Methane
CHP	Combined Heat and Power
CL	Chicken Litter (also Poultry Litter)
Cl	Chloride
Cl_2	Chlorine
cm	Centimeter
CO	Carbon Monoxide
$CO(NH_2)_2$	Urea
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
$COD/m^3/d$	Chemical Oxygen Demand per cubic meter per day
CO_x	Carbon Oxides
CV	Calorific Value
DAF	Dry Ash Free
DECC	Department of Energy and Climate Change

EC	European Commission
ELV	Emission Limit Value
EPR	Energy Power Resources
eq.	Equivalent
EU	European Union
F	Fluorine
FAO	Food and Agriculture Organisation of the United Nations
FBC	Fluidised Bed Combustor
FBT_1	Freeboard Temperature at 0.24 m above the static bed (°C)
FBT_2	Freeboard Temperature at 0.53 m above the static bed (°C)
FC	Fixed Carbon
Fe	Iron
$Fe(SO_4)_3$	Ferrous Sulphate
Fe_2O_3	Ferric oxide
$FeCl_3$	Ferric Chloride
$FeCO_3$	Iron Carbonate
FeO	Ferrous Oxide
FeS	Ferrous Sulfide
FP	Framework Programme
FV	Fluidising Velocity
g/kW	grams per kilo Watt
GCV	Gross Calorific Value
GHG	Greenhouse Gas
GJ	Giga Joule
Gt	Giga tonnes
GWh	Giga Watt hour

H	Hydrogen (Atomic)
H_2	Hydrogen (Gaseous)
H_2O	Water
H_2S	Hydrogen Sulfide
H_2SO_4	Sulphuric Acid
HCG	Hollandase Constructive Group
HCl	Hydrochloric Acid
HCN	Hydrogen Cyanide
HGG	Hot Gas Generator
HHV	Higher Heating Value
HL_1	Heat loss between bed (BT) and freeboard temperature (FBT_1) measurement points
HL_2	Heat loss between freeboard temperatures FBT_1 and FBT_2 measurement points
hr	Hours
I	Alkali Index I
ID	Inside Diameter
IEA	International Energy Agency
INETI	Instituto Nacional de Engenharia, Tecnologia e Inovação
IPCC	Intergovernmental Panel on Climate Change
K	Potassium
K_2CO_3	Potassium Carbonate
$K_2Fe_2O_4$	Potassium Ferrite
K_2O	Potassium oxide
K_2O_4	Potassium superoxide
K_2PO_4	Potassium phosphate
K_2S	Potassium sulfide

$K_2Si_4O_9$	Potassium Tetra silicate
K_2SiO_3	Potassium Silicate
K_2SO_4	Potassium Sulphate
K_3PO_4	Potassium Phosphate
KCl	Potassium Chloride
kg	kilogram
kg/GJ	kilogram per Giga Joule
kg/h	kilograms per hour
kg/Nm^3	kilogram per Normal cubic meter
kg/s	kilograms per second
kgf/cm^2	kilogram (force) per square centimetre
kJ	kilo Joule
KOH	Potassium Hydroxide
kPa	kilo Pascal
kW	kilo Watt
kW/m^2	kilo Watt per square meter
kWe	kilo Watt Electric
l/h	litres per hour
l/h	litres per hour
l/min	litres per minute
lb	Pound (mass)
LCPD	Large Combustion Plant Directive
LHV	Lower Heating Value
LL	Lower limit
m/s	meter per second
m^2/g	meter square per gram

m^3	Cubic meter
m^3/h	Cubic meter per hour
mbarg	milibar gauge (pressure)
MBM	Meat and Bone Meal
mg/Nm^3	miligrams per Normal Cubic meter
$Mg_3(PH_4)_2$	Magnesium Phosphate
$MgCl_2$	Magnesium Chloride
$MgCO_3$	Magnesium Carbonate
MgO	Magnesium Oxide
MgOH	Magnesium Hydroxide
$MgSO_4$	Magnesium Sulphate
min	mintues
MJ	Mega Joule
MJ/kg	Mega Joule per kilo gram
mm	millimeter
mmWg	millimeter water gauge
MP	Melting Point
MSW	Municipal Solid Waste
MW	Mega Watt
MWe	Mega Watt Electrical power
MWh	Mega Watt hour
MWth	Mega Watt Thermal
N	Nitrogen (Atomic)
N_2	Nitrogen (gaseous)
N_2O	Nitrous Oxide
Na	Sodium

Na_2CO_3	Sodium Carbonate
Na_2O	Sodium Oxide
Na_2S	Sodium Sulfide
Na_2SO_4	Sodium sulphate
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NCO	Isocyanate radical
NCV	Net Calorific Value
NH	Ainido group radical
NH_3	Ammonia
NH_4HCO_3	Ammonium bicarbonate
Nm^3/kg	Normal cubic metre per kilogram
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_x	Oxides of Notrogen
O	Oxygen (Atomic)
O_2	Oxygen (gaseous)
OH	Hydroxyl radical
P	Phophorous
P_2O_5	Phosphorous Pentoxide
PP	Pressed pulp
ppm	parts per million
R	Mixing ratio
RDF	Refuse Derived Fuel
RHI	Renewable Heat Incentive
RO	Renewable Obligation

S	Sulphur
SBP	Sugar Beet Pulp
sec	second
SEM	Scanning Electron Microscopy
Si	Silica
SiO_2	Silicon dioxide
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SRES	Special Report Emission Scenarios
SSB	SAACKE Swirl Burner
t/y	Tonnes per year
TGA	Thermo gravimetric analysis
Ti	Titanium
TiO_2	Titanium Dioxide
tpa	tonnes per annum
TPH/tph	Tonens Per Hour
T_s	Sintering Temperature
UK	United Kingdom
U_{mb}	Minimum bubbling Velocity
V	Volatiles (also atomic symbol for Vanadium)
VOC	Volatile Organic Compound
w.b	wet basis
W/m^2K	Watt per square meter per Kelvin
WC	Wood Chips
wt	Weight
λ	Excess Air Factor

Chapter 1

Introduction

1.1 Climate change

Greenhouse gas (GHG) emissions are on the rise despite investment in energy intensive technologies as well as efficiency improvements. The emissions increased by 1.6% per year on average, over the last three decades. Carbon dioxide emissions resulting from the combustion of fossil fuels are increasing at a rate of 1.9% [Rogner, *et al.* 2007]. According to the fourth assessment report of the IPCC, in 2030 more than 80% of the global energy mix will be from fossil fuels with consequent GHG emission implications if energy policies are not substantially changed. The energy related CO_2 emissions are projected to be 40 – 110% higher in 2030 as compared to 2000.

United Kingdom CO_2 emissions by fuel use are given in Figure 1.1 [DECC, 2012a]. The figure shows that in 2011, the emissions from the use of gas has increased by 32.8% while from the use of oil and coal have decreased by 22.9% and 53.6%, respectively, over 1990 levels. The figure shows that total CO_2 emissions in 2011 decreasd by 22.7% over 1990 levels. Comparison of CO_2 emissions from different fuels in 1990 and 2011 is given in Figure 1.2. The figure shows that during this period percentage emisions from coal decreased, those from gas increased while from oil remained almost constant.

According to fourth assessment report of the IPCC [IPCC fourth Assessment Report, 2007] global green house (GHG) emissions will continue to grow over the next few decades under current climate change mitigation policies and related sustainable development practices. The SRES scenarios, Figure 1.3, [Special Report: Emissions Secnarios, 2000] projections indicate that baseline GHG emissions will incease by a range of 9.7 to 36.7 Gt of CO_2 (eq.) i.e. 25 to 90%, between 2000 and 2030. According to the projections, by 2030 and beyond, fossil fuels are going to play a dominant role in the global energy mix.

Recently UK Government has announced its plans for the delivery of the Renewable Heat Incentive (RHI), launched in November 2011, including a time table setting out what the UK Government is intending to do and when for both the domestic and non-domestic sectors. According to the time table, in November 2012, longer term cost control regulations, air quality and biomass sustainability proposal are going to be laid in the UK Parliament for debate. Following the debate, the Government intends to implement the longer term cost control policy by the end of this financial year (2012), and biomass sustainability standards by mid March 2013 [DECC, 2012b].

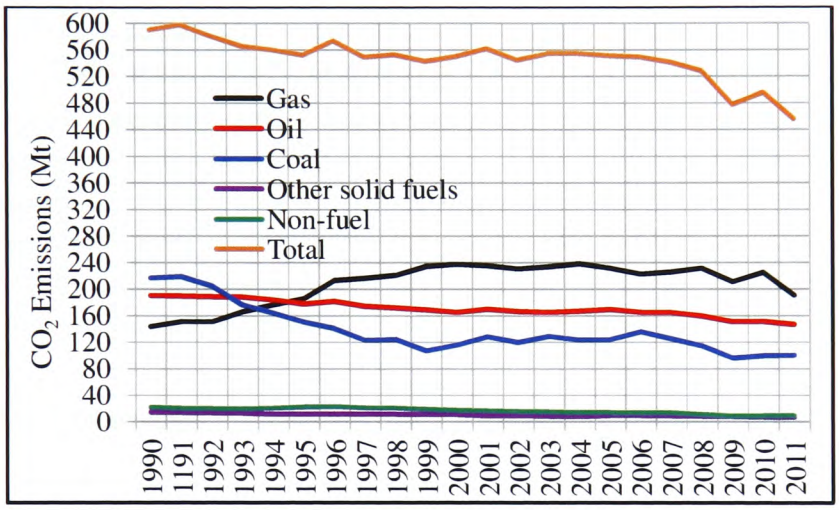
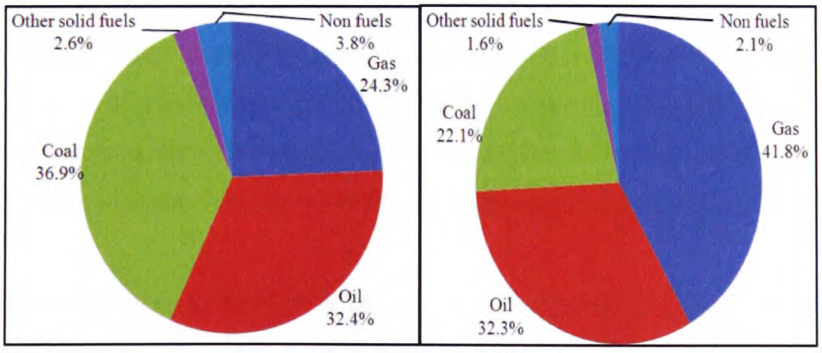


Figure 1.1: United Kingdom CO_2 emissions by fuel (1990 – 2011*) [DECC, 2012a, Table 8]

*At the time of publication (April 2012), 2011 figures are provisional



(a) 1990 (b) 2011

Figure 1.2: United Kingdom percent CO_2 emissions by fuel(1990 and 2011) [DECC, 2012a, Table 8]

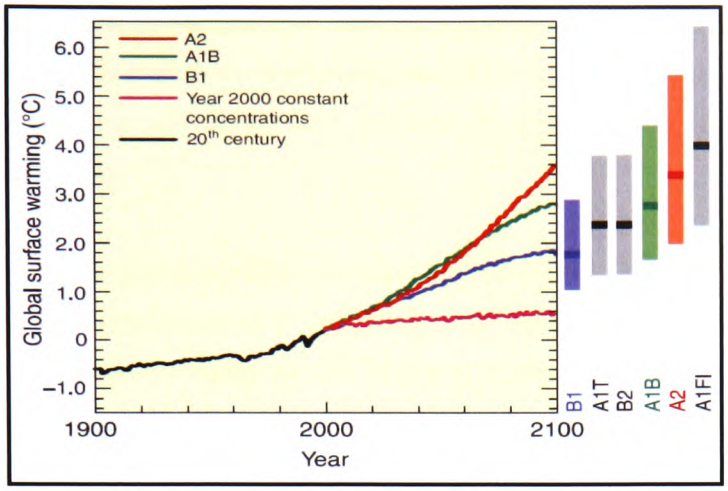


Figure 1.3: Global surface warming projections [IPCC Fourth Assessment Report, 2007]

Solid lines are multimodel global averages of surface warming (relative to 1980 – 1999) SRES Scenarions [IPCC Special report on Emission Scenarios (SRES), 2000] A2, A1B and B1 shown as continuations of the 20th century simulations. The range line is for he experiment where concentrations were held conatnt at year 2000 values. The bars in the middle of the figure indicate the best estimate (solid line with in each bar) and the likely range assessed for the six SRES scenarios at 2090 – 2099 relative to 1980 – 1999. The assessment of the best estimate and likely ranges in the bars includes the Atmospheric-Ocean General Circulation Models (AOGCMs).

1.2 Importance of Biomass:

Humankind has a long history of using biomass for cooking and heating purposes. The use of wood is thought to be much older than civilisation. In third world countries where the majority of the population lives in villages with no access to natural gas, wood is still the primary source of their energy source and to fulfil their everyday needs. Biomass is considered to be CO_2 neutral as during its growth it uses the equivalent amount of CO_2 that is then emitted during its combustion. Of course there is an energy penalty associated with its harvesting and transportation etc and some body can argue on the CO_2 neutrality of biomass. Nevertheless, using biomass for power production can significantly reduce GHG emissions.

Use of biomass for power generation is getting increased attention but most of the work is limited to easy biomass fuels such as clean wood. Limited attention has been paid to difficult biomass fuels particularly by-products of industrial process such as meat and bone meal from meat industry, sewage sludge from waste water treatment industry, pressed sugar beet pulp (PP) from sugar industry etc. The biomass materials originating from process industries can

be used to produce onsite power and thus limit their dependence on the national grid. This will not only reduce CO_2 emissions emitted by burning fossil fuels to provide power to run these industries but also will solve their problem of utilisation of these materials in environment friendly way.

In April 2002, UK government brought into effect the Renewable Obligation (RO) which is an "obligation on electricity suppliers to source a specific and annually increasing proportion of electricity from eligible renewable sources or pay a penalty" [MacLeay *et al.* 2011]. The intention is to provide incentive to increase renewable production to help meet targets set out for climate change. As a result co-firing of renewables with fossil fuels increased by 39% from 1086 GWh in 2009 to 2506 GWh in 2010, with 29% increase in biomass from 297 MWh. Total power production from biomass sources in 2010 remained 12% higher than in 2009 levels. The UK distribution of renewable energy by fuel use during 2010 is given in Figure 1.4. The figure shows that the largest contribution to renewables in terms of input is from biomass (83%). Distribution of renewable energy from three main sources, hydro, biomass and wind, from 2000 to 2010 is given in Figure 1.5. The figure shows that overall proportion of energy form hydro has decreased while from biomass and wind has increased. Energy production from biomass in 2010 is about three times of that in 2000 [MacLeay *et al.* 2011].

Energy value of biomass materials is different from that of coal thus combustors designed for coal are not suitable for biomass combustion without energy efficiency and environmental penalty. This leaves us with two options, either design dedicated biomass combustion systems or co-fire biomass with a primary fuel (coal) in combustors designed for coal. However, there is a limit on maximum biomass proportion which can be successfully burned with coal without drastically affecting combustion phenomenon. The proportion of biomass in blend with coal varies from biomass to biomass depending upon their characteristics.

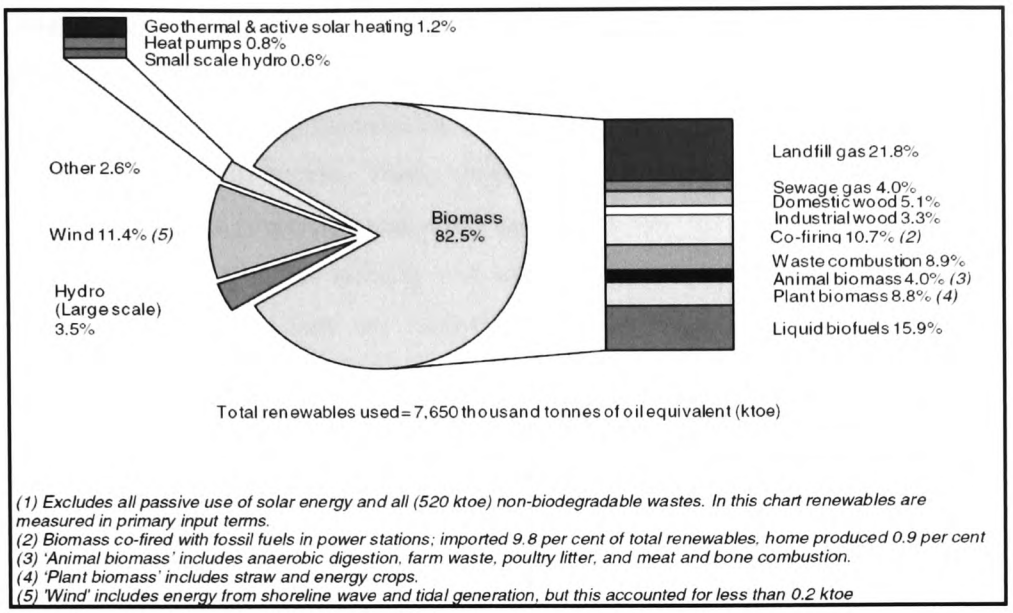


Figure 1.4: Renewable energy by fuel use in UK in 2010

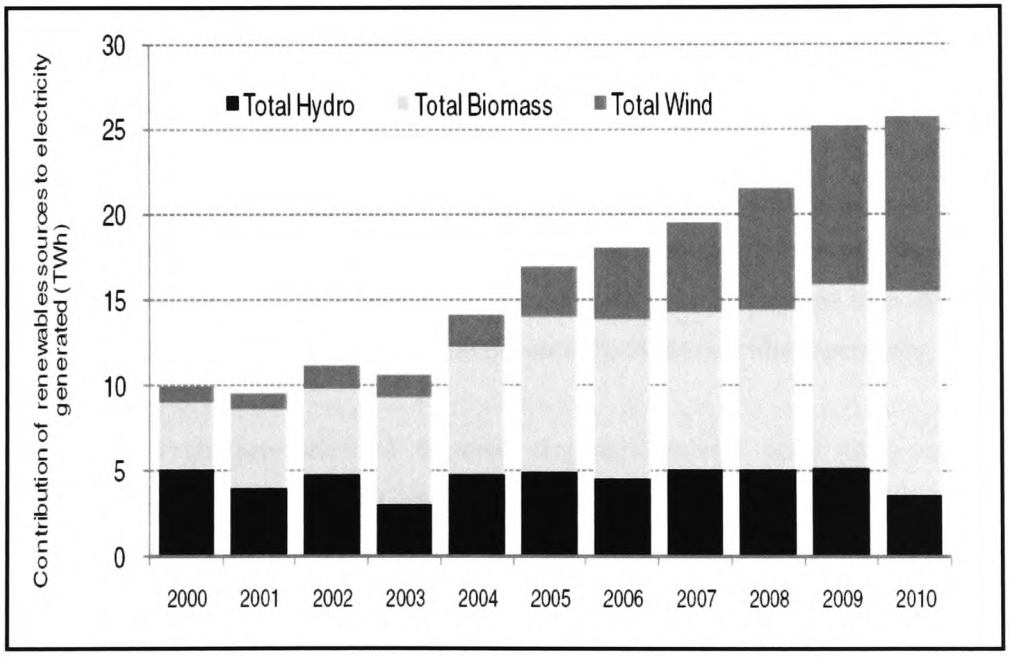


Figure 1.5: Electricity generation by main renewable source in UK (2000 – 2010)

The combustion of biomass is widely recognised to be a means of reducing carbon dioxide emissions from heating processes. However one of the main barriers to the more widespread application of the technology has been the difficulty of burning relatively cheap, poor quality, unprepared biomass materials. These unprepared potential fuels can be variable in composition and fuel properties and often have relatively low calorific values and high moisture content so that the stability and efficiency of the combustion process can be adversely affected unless they are co-fired with a hydrocarbon support fuel. There is, however, a lack of information on the "optimum" conditions for co-firing of coal and high moisture biomass as well as on the proportions of support fuel which should be used in particular applications.

The sugar making process, discussed in Chapter 3, produces by-products e.g. vinasse, raffinate and pressed sugar beet pulp.Vinasse and raffinate are liquid while Pulp is a solid by-product. After sugar extraction, remaining beet is pressed mechanically to remove water which results in pressed sugar beet pulp having 20 – 24% dry matter. Raffinate and vinasse originate from the liquid stream after sugar, alcohol and betaine are taken out. All these by-products have an energy value associated with them which can be recovered by employing a suitable combustion technology. As a result of the high moisture content which is of the order of 50 – 75%, it may not be possible to combust these materials without the use of a primary fuel, such as coal, having a high calorific value to compensate for the energy loss due to the presence of excessive amounts of water. Moreover, it may not be possible to combust these materials in conventional systems without major modifications or without penalties.

The combustion characteristics of biomass materials depend upon their origin e.g. combustion of clean wood may be much easier, efficient and environmentally friendly as compared to the combustion of industrial sludge. While the wood can be combusted in conventional combustion systems, industrial sludge, for example, cannot be burned without designing a specific combustion system. Different combustion systems such as grate type, stoker type, pulverised fuel type and fluidised bed combustion systems are used to deal with different kinds of fuels and are chosen depending upon the fuel characteristics and application.

Fluidised bed combustion is a promising technology for burning fuels of widely different qualities including industrial wastes and by-products which are very difficult to burn in conventional combustors. The technology has been widely used for firing single fuels such as wood, sludge, and combination of these fuels with coal.

Because of the agricultural origin of these by-products they contain alkali metals which may cause problems during combustion. Agglomeration of the fluidised bed material could be a potential problem due to the presence of alkalis particularly potassium (K). Potassium is known for its role in making eutectic blends with silica (Si) having lower melting points.

1.3 Problem Statement:

This project was carried out in conjunction with British Sugar Plc. They have a coal fired Hot Gas Generator (HGG) at their Cantley site. The design capacity of the HGG is 40MW but it is underperforming and is limited to 24MW due to restricted air flow through its sparge pipe system. The hot gases from the HGG are used to dry sweetened pressed sugar beet pulp to make animal feed. Because the HGG is not able to run at its full capacity, some of the pressed pulp is dried in an oil fired dryer. However, the oil is very expensive so that British Sugar wants to enhance the performance of the HGG to reduce dependence on oil for their animal feed drying purposes.

Two of the options to solve this problem are either to increase air flow or to cool the bed. Air flow to the bed can be increased by reducing resistance through sparge pipes. Cooling of the bed can be achieved by introducing moisture into the bed. Previously, efforts have been made to redesign the sparge pipes system but they have not proved to be very successful. Therefore, this study is aimed at looking into the second option i.e. cooling the bed by introducing moisture. The injection of water into the bed can be achieved by either co-firing high moisture biomass with coal or introducing water into the bed. Both of the options have been employed during this study. By using either of these two options, the excess air required for getting a stable bed temperature is found to be reduced.

High moisture biomass i.e. vinasse, raffinte and presses sugar beet pulp are available on site. Therefore, it was decided to assess the feasibility of co-combustion of these biomass

materials with coal in the fluidised bed. Due to their agricultural background these materials contain considerable amounts of alkalis, especially potassium, in them. The content of potassium is very much higher in vinasse and raffinate as compared to pressed pulp thus vinasse and raffinate are more prone to cause agglomeration during fluidised bed combustion as compared to pressed pulp. Therefore, the major part of this study was dedicated to co-firing pressed sugar beet pulp with coal.Part of the study was also dedicated to assess the agglomeration behaviour of the sugar by-products when co-fired in fluidised bed.

1.4 Aims and Objectives:

The main aim of this research work is to carry out the feasibility of increasing thermal capacity of Hot Gas Generator (HGG) at British Sugar's Cantley site. The capacity of the HGG is limited by the flow of fluidising gases. It is thought that if the bed is cooled, its capacity can be increased by introducing more coal. The idea behind this is that the cooling of the bed will spare some of the excess air to be used to combust extra coal. In order to prove this hypothesis two different techniques have been employed i.e. injection of water into the bed stabilised at high temperature and use of high moisture biomass to provide cooling effect. The fuels tested are those originate from sugar industry at different stages of sugar production process. Objectives of the project are listed below.

- Performance of the fluidised bed test rig, described in Chapter 3, is evaluated by measuring different operational parameters

- Pollutant emissions i.e. SO_2, NO_x, CO and CO_2 are measured during firing and co-firing of different fuels and has been analysed and compared

- Bed and freeboard temperatures are measured and temperature profiles are plotted against excess air for different tests

- Air flow and fuel flow rates are measured and stoichiometric calculations are performed

- Thermal input data, bed and freeboard temperatures are used to calculate Efficiency of the system for different fuels/fuel combinations

- Effect of different operational parameters and fuel characteristics on combustion performance is evaluated

- Effect of moisture in fuel on the excess air requirement for a set bed temperature and thus possibility of enhancing the capacity of the underperforming 40MW Hot Gas Generator (HGG) at British Sugar's Cantley site is evaluated

- Water injection tests at different water flow rates and coal inputs are also performed to assess its effect on bed cooling. Emissions data is measured and compared to find out the possibility of occurring water gas reaction

- Tendency of biomass fuels to cause agglomeration during fluidised bed combustion is pre-assessed by calculating agglomeration indices

- Muffle furnace tests of different combinations of fuels (raffinate and vinasse) and sand at different temperatures and times are performed to evaluate their behaviour during combustion in a fluidised bed

- Fluidised bed combustion tests are performed with the biomass fuels (raffinate, vinasse and pressed sugar beet pulp) and coal and/or natural gas to assess their agglomeration behaviour

1.5Structure of the Thesis:

Chapter 1 provides the introduction to the thesis. It covers the importance of the project, climate change and global warming, importance of using biomass to tackle the global warming, importance of fluidised bed technology for power sector. It also highlights main reasons for carrying out this research work. Finally it gives brief overview of the thesis.

Chapter 2 includes literature review, specifically covering combustion of high moisture biomass materials. It discusses combustion of high moisture by-products from different industries including sugar industry, meat industry, waste water industry etc. Particular attention has been given to cover the combustion of high moisture fuels in fluidised beds wherever available.

Chapter 3 includes materials and methods used to perform tests. Schematic of the fluidised bed, design parameters, control parameters and its operational procedures are described in detail. Calibration of solid feeder and liquid pump is also described. Principles of feeding solid and liquid fuels into the bed are also discussed. As a major part of this study involves sugar making process by-products, the sugar making process is also briefly described in this chapter in order to show the origin of these by-products.

Chapter 4 gives details of commissioning and preliminary testing of the fluidised bed test rig. It includes rig commissioning and characterisation on natural gas and tests with gas oil and co-firing emulsions of gas oil in water with natural gas. Energy balance on natural gas tests has been described.

Chapter 5 discusses main combustion tests including firing and co-firing of Thoresby coal with different biomass fuels e.g. wood pellets, wood chips (WC) and pressed sugar beet pulp. It gives bed and freeboard temperatures as well as self defined fluidised bed efficiency calculation results at different power inputs and excess air levels. Effect of fuel characteristics particularly moisture content as well as different operational parameters on the performance of the fluidised bed are discussed.

Chapter 6 discusses emissions from combustion tests described in Chapters 4 and 5. Emissions of NO_x, SO_2 and CO are discussed in relation to operational parameters e.g. fuel moisture, bed temperature, excess air, measurement point etc. Effect of co-firing on the emissions performance of the rig is also discussed.

Chapter 7 discusses bed agglomeration. It covers causes of agglomeration, agglomeration mechanisms and agglomeration control strategies. Agglomeration indices which can predict the behaviour of fuelswhen combusted in a fluidised bed are also described and calculated for

the fuels tested. Muffle furnace tests of raffinate and vinasse blends, with sand in different proportions, to pre-assess their behaviour during combustion in fluidised bed are also described in this chapter. Results of agglomeration tests with vinasse, raffnate and pressed sugar beet pulp in co-combustion with coal and natural gas (in some cases) are described and discussed. It also discusses SEM analysis of bed samples taken after firing the rig with different fuels.

Chapter 8 describes water injection tests for coal firing as well as natural gas firing. It discusses the effect of water injection on bed temperature and thus air requirement to achieve a set bed temperature at a particular power input. Effect of water on combustion performance due to poor air fuel mixing and potential towards water gas reaction is also discussed.

Chapter 9 gives conclusions and recommendations. Conclusions are drawn from the study and discussions described from Chapter 4 to Chapter 8. The recommendations are made based on the conclusions and observations made during the tests as well as discussions in previous chapters and data analysis.

Chapter 2
Literature review

2.1 Introduction:

There is increasing concern with regard to global climate change and this can be blamed on man-made (anthropogenic) processes or natural causes. Emissions of green house gases (GHG) by burning fossil fuels are a particular worry so that coal burning utilities are being encouraged to reduce production of carbon dioxide through use of renewable "carbon neutral" fuels such as biomass [Boylan *et al.* 2000]. Moreover biomass dumping to landfill and subsequent emission of methane is also a contributor to climate change. Consequently combustion of biomass for energy purposes not only reduces carbon emissions and the amount of these materials sent to landfill but can also give economic advantages.

The Kyoto Protocol obliges countries to reach between 2008 and 2012, an 8% reduction in GHG emissions compared to 1990 levels [Silvia *et al.* 2008]. Biomass may be one of the largest contributors in order to meet the UK target of 20% of electricity from renewables by 2020 and to cut CO_2 emissions by 60% by 2050 [The Energy White Paper, 2007]. The Secretary of State for Energy and Climate Change announced on 14th March 2011 to cut EU emissions by 30% by 2020. The Secretary of State and 6 other European environment ministers have asked for tougher climate targets to ensure that emissions are reduced by 80% by 2050 [DECC, 2011].

Biomass is often cheaper than alternative fossil fuels and is most of the time easily available. Biomass can include traditional non fossil fuels such as wood and wood waste or straw, herbaceous biomass, agricultural wastes, industrial wastes etc. sometimes called new biomass [Arvelakis, and Frandsen, 2007]. Waste fuels such as Refuse Derived Fuels (RDF) and plastics are characterised by high chlorine (Cl) and low sulphur (S) content, high alkaline, heavy metals and inert materials [Elmar, 2007]. In addition to the use of "wastes" there is also a tendency towards producing dedicated crops to produce energy from biomass. Across

the EU the installed capacity of biomass/waste fuelled plants is forecast to grow from around 4.4 GW in 2000 to 6 GW in 2020 [EC, 1999].

Biomass is a fuel that varies considerably in bulk density, net calorific value (CV_s) and moisture content. It has less carbon and more oxygen than coal which results in its lower heating value [Hein and Bemtgen, 1998]. Biomass fuels are highly volatile and the reactivity of the char is also high. Combustion of biomass needs to be conducted at high excess air levels because of sudden de-volatilisation of these fuels and proper air control is required to improve the combustion process [Srinivasa Rao 2007]. The variable nature of biomass fuels can make it difficult to devise a suitable combustion system and combustion of high moisture content biomass (as is the main subject of this thesis) is a particular challenge because of its low calorific value (CV). An auxiliary source of energy is usually required so that this thesis considers the co-combustion of high moisture biomass with coal.

Different techniques and combustion systems are available for the combustion of such blends of fuels with sometimes widely different characteristics. For example fluidised bed combustion of blends of coal and biomass has been studied over a limited range of biomass fractions. Coal is a relatively cheap fuel particularly with respect to oil so that co-firing of coal with biomass has been successfully applied in for example, bagasse and coal co-firing in two 31 MW_e power plants at Saint-Louis, La Reunion.

This literature review discusses the combustion properties of high moisture content biomass materials (particularly some of those arising as co-products in the sugar industry) and appropriate combustion systems are also discussed. The experimental work is concerned with fluidised bed combustion so that the use of this technology has been looked at in detail. Agglomeration of the bed can be a potential problem with biomass in fluidised bed combustion systems and this topic is discussed in Chapter 7 of this Thesis.

2.2 Combustion phenomena and combustion systems:

Technically combustion is a complex process involving high reaction rates, high heat release, many reactants and reaction schemes [Peter *et al.* 1999]. The most difficult aspect of the combustion process is the initial ignition, biomass materials generally require a temperature

of around 236 – 270 °C for ignition [Vamvuka *et al.* 2011]. Once started, the process is self sustaining provided sufficient air is provided for combustion. During the combustion process the chemical energy of the fuel is converted into thermal energy which is available in the form of the hot flue gas which can be used for different applications. Part of the energy that is not converted into "useful" flue gases is lost and is usually termed as "heat losses" and is responsible for the lower efficiency of the combustion process. These heat losses can be broadly divided into losses through walls, losses due to hot ash removal, unburned particles in the ash and unburned pyrolysis gases and carbon monoxide (CO) in the flue gases [Peter *et al*, 1999] and (sensible + latent) heat of water in the flue gas rejected to atmosphere.

In the combustion of solid fuels there are two distinct combustion phases. In the first phase gas phase reactions take place when volatiles are released from the fuel as gases. This phase is often termed as flaming combustion. In the second phase chemical reactions take place at the surface of the solid fuel, termed as char combustion. Diffusion of oxygen on the solid surface is inhibited by, firstly, the volatiles flowing away from the particle and, secondly, by use of oxygen by these volatiles. Thus combustion of char is thought to be initiated once the combustion of volatiles nears completion [Shanmukharadhya. and Sudhakar 2007]. However, Peter *et al*, (1999) suggest that combustion of biomass takes place in four distinguishable steps. In the first step known as "drying" water is evaporated from the fuel. In the second step biomass is thermally degraded into volatile gases and solid char. This step is called "pyrolysis and reduction". The third step "combustion of volatiles" involves the burning of volatile gases above the fuel with a yellow flame. Fourth step is the "burning of char" in the fuel bed with a small blue flame or glowing of char particles.

The theoretical air requirement for the combustion of a fuel depends upon the composition (proximate and ultimate analysis) of the fuel. For complete combustion more than the theoretically required amount of air must be fed to the system. The ratio of total air fed to the system to that of theoretical air requirement is termed as the excess air factor (λ). The Adiabatic and actual flame temperatures in a combustor decrease with increasing λ. Theoretically, the maximum flame temperature can be achieved at $\lambda = 1$. However, practical combustion systems are always operated at $\lambda > 1$ to ensure complete combustion. Optimum value of λ depends upon fuel properties, design of the combustor and operating conditions. In well designed systems the value of λ for wood is between 1.6 and 2.5 while in poorly

designed systems it may be as high as 4 or even 5 [Peter *et al*, 1999]. The Size and uniformity of the fuel particles is one of the factors determining the combustion performance of solid fuels and these can be pre-treated to get a relatively uniform particle size but at some extra cost [Peter *et al*, 1999]. To achieve high performance and lower emissions combustion systems must be operated continuously and at designed loads [Nussbaumer, 1991].

Combustion systems for solid fuels and biomass materials can be broadly categorised as fixed bed, moving bed and fluidised bed types. Fixed bed systems include manual feed systems, spreader-stoker systems, under screw systems, through screw systems, static grates and inclined grates. Typical combustion temperatures in fixed grate systems range from 850 °C to 1400 °C [Peter *et al*, 1999]. The Moving grate is an example of moving bed systems. However, only fluidised bed systems will be discussed in detail in this chapter since this type of combustor is applied in the current experimental study.

2.3 Fluidised bed combustion:

Fluidisation is defined as the operation through which beds of fine solids are transformed into a fluid like state through contact with a gas or liquid [Levi, 1991]. In 1960s Douglas Elliott promoted the use of coalfired fluidised beds for generating steam with the British Coal Utilisation Research Association (BCURA) and the National Coal Board of the UK [Howard, 1983]. Shortly after Elliott's initial work, a fluidised bed development program started at Central Electricity Generation Laboratory, Marchwood [Basu, 2006]. Fluidised bed systems comprise a combustion chamber, maintained at 700 – 1000 °C, containing a sand bed acting as a heat transfer medium. The fuel is largely burnt in this bed. The bed is fluidised by blowing air or combustion products with high oxygen content through a perforated bottom plate or distributor to force the bed material upward and keep it in suspension. Depending upon the fluidising velocity the bed can be defined as bubbling or circulating [Peter *et al*, 1999].

A bubbling fluidised bed is divided into two parts with an initial zone containing freely moving sand particles supported by upward blowing air creating the impression of a bubbling fluid and a second zone above the bed called the freeboard [Peter *et al*, 1999]. The height of the freeboard is an important factor for determining the overall performance of a fluidised

bed combustion system since unburned fuel particles elutriated from the bed and volatiles released from the fuel continue to burn in the freeboard and require a residence time of 1 – 2 seconds to complete combustion [Anthony, 1995]. The performance of the combustion process can be improved by properly controlling the air to fuel ratio, ensuring good mixing of air and fuel, maintaining a residence time of more than 1.5 sec and bed temperature of above 850 °C [Peter *et al*, 1999]. Bubbling fluidised beds offer one of the most convenient means of solid-gas interaction due to good mixing and high heat and mass transfer rates.

Fluidised beds have the advantage of being able to operate with higher residence times with lower fluidisation velocity. Their main drawback is the risk of ash sintering and bed agglomeration causing de-fluidisation due to low temperature ash derived eutectics that stick bed particles together. Sintered ash also causes the formation of deposits on heat exchanger surfaces reducing their effectiveness. Sulphur can combine with molten alkali sulphates that stick and corrode heat transfer surfaces [Fryda *et al.* 2006].

In a circulating fluidised bed the velocity of the air or fluidising medium is so high that bed and light fuel particles flow upward with the gas stream out of the combustor before subsequent separation in a cyclone prior to return back to the combustor. Light fuel particles burn during circulation, while, heavy fuel particles burn in the bed until they are light enough to be lifted by the air velocity to join the circulation stream. The circulation rate is increased to accommodate high CV fuels and this increases the flexibility of the system. If the bed temperature is below 850 °C, combustion is incomplete and unburned hydrocarbons are emitted along with tars. This is particularly true for high moisture content (> 50%) fuels particularly where combustion air is not preheated. The fuel can be dried to improve performance but this involves extra costs [Peter *et al*, 1999].

The Ahlstrom group in Finland started development of Bubbling Fluidised Beds (BFB) in 1960s. Biomass fired Bubbling Fluidised beds started in 1982 with the design of a 10t/h BFB for steam generation fired with rice husk in India. Since then many BFB have been designed and operated on different fuels and BFB has taken over from the stoker fired boilers of the past. The first 84 MW, Circulating Fluidised Bed (CFB) combustor was built, exclusively for steam and heat, in Vereingte Aluminum Werke at Luenen, Germany in 1982 [Basu, 2006].

Fluidised bed combustion has been extensively studied and applied to both coal and biomass combustion systems. For example, the technology is applicable to a wide range of agricultural residues due to its inherent advantage of fuel flexibility, low operating temperature and isothermal operating conditions [Levi, 1991]. Fluidised bed combustion is a fully developed technology for solid fuels [Baron, *et al.*, 2002] but most of the time is limited to low moisture solid biomass and combustion of high moisture solids and liquids (particularly industrial wastes) has received less attention despite being technically feasible. Fluidised bed combustors have been applied in boilers and hot gas producers since they are capable of efficiently burning a wide range of fuels [Garwood, 2007] and as stated by McDonnell, (2001) the flexibility of FBC with regard to the nature of the fuel makes it very suitable to use the system for both mono- and co-combustion processes. Although more attention has been paid to solid fuel fluidised bed combustors can be designed to combust almost any solid, semi-solid or liquid fuel without the use of supplementary fuel as long as the heating value of the fuel is sufficient to heat the fuel, drive off the moisture and preheat the combustion air. With appropriate attention to fuel preparation, blending and operating procedures wastes can be co-fired with coal in existing fluidised bed combustors. Conversion of existing fluidised bed combustors to co-firing systems is more cost effective and efficient than building a dedicated new unit [McGowin and Howe, 1994].

A fluidised bed is of particular interest in co-combustion studies because of its fuel flexibility, high combustion efficiency, in-situ sulphur removal and low NO_x emissions [Basu, 2006]. During co-combustion the properties of the base fuel e.g coal (representing more than 25% by energy fraction) dominate the emission picture [Leckner *et al.* 2004]. FBC is capable of converting fuels completely at lower temperature levels (750 – 900 °C) compared to conventional combustion systems, while it offers the possibility to use bed material additives to reduce emission levels [McDonnell K. *Et al* 2000]. Fluidised beds can accommodate fuels with up to 60% moisture content and up to 50% ash content. Process integrated emission control technology of CFB replaces further flue gas cleaning in most applications and reduces investment and operational costs. Although coal fired fluidised bed combustion is a mature technology it is more problematic with biomass and operational problems can occur [Olofsson, *et al.* 2002].

This thesis is concerned with co-firing of coal with high moisture biofuels so that it is relevant at this stage to review briefly a number of past projects on so-called co-combustion.

2.4 Co-Combustion:

Co-combustion is essentially the combustion of two or more fuels in combination and in this particular thesis is mainly concerned with the combined combustion of biomass and coal. Co-combustion is of particular interest because it provides efficient means of combusting high moisture, low CV biomass materials and reduces SO_2 and NO_x emissions. Biomass co-firing reduces sulphur emissions [Suksankraisorn *et al.* 2003], because virtually negligible sulphur in some biomass materials and enhanced sulphur retention in ash [Basu, 2006] and reduces NO_x emissions due to lower combustion temperatures and the lower nitrogen (N) content of many biomass materials. Typical proximate, ultimate and ash analysis of some of the biomass fuels are given in Appendix A.

In the EU a number of projects on the co-combustion of biomass and coal has been or are being carried out e.g. APAS, CoPower, IEA Bioenergy Task 32 etc. APAS (Activite de Promotion, D'Accompagnement et de Suivi) continued from 1992 to 1994 and was an EU clean coal technology programme which was concerned with co-firing in both fluidised bed and pulverised fuel boilers from laboratory to full scale. Up to 75% reduction in SO_2 emissions was observed and was attributed to lower Sulphur content of biomass as well as Sulphur retention in the ash [European Bioenergy Networks, 2003]. CoPower (part of FP6) involving 10 organisations from 6 countries concentrated on the production of energy from biomass and non-toxic sources. It is using fluidised bed combustion technology to investigate the environmental implications of different fuels (two different coals, 3 types of biomass and 2 kinds of waste materials) and the operational aspects. Under this project the socio-economic impact of the proposed system will be assessed by performing a complete environmental impact and life cycle assessment. The so-called Task 32 looks at the use of biomass combustion for heat and power generation, with special emphasis on small and medium scale CHP plants and co-firing of biomass with coal in traditional coal-fired boilers ranging from 5 to 700 MWe. In addition with the participation of 25 partners from eight EU countries a two year project "Combined Combustion of Biomass/sewage sludge and coals of high and low

rank in different systems of semi-industrial and industrial scale" which started in 1993 considered fluidised bed combustion from laboratory rigs to large scale utility boilers.

Biomass has been successfully co-fired with coal on industrial scale but share of biomass in the combined fuel is very low. Co-combustion of biomass with coal has been studied in the past and few articles are available in open literature. Co-combustion of switch grass [Boylan *et al.* 2000], cattle feedlot [Ross *et al.*2002], hardwood and softwood [Harding and Adams 2000], meat and bone meal [Fryda *et al.* 2006], municipal solid waste [Suksankraisorn *et al.* 2004; Ducarne *et al.* 1998; Dong *et al.* 2002; Suksankraisorn *et al.* 2003], wood chips [Nevalainen*et al.* 2007], olive oil waste [Suksankraisorn *et al.* 2003; Armesto *et al.* 2003] and sewage sludge [Leckner *et al.* 2004] among others have been reported.

Although considerable effort has been made there are still technical barriers to the large scale application of biomass as a fuel either alone or in combination with other fuels. Biomass has significantly different properties which may have impact on the combustion process. For example high amount of alkali metals, chlorine and sulphur are responsible for corrosion. In the following combustion and co-combustion of different high moisture biomass/waste materials has been reviewed.

2.5 High Moisture Biomass Combustion:

Biomass fuels are usually wet and the flue gas produced by combusting biomass may contain large amounts of water vapour and hence latent energy [Peter *et al*, 1999]. It is well known that changes in moisture have an important impact on the burning rate of fuels and high moisture levels in fuels can cause ignition difficulties [Yang *et al.* 2003]. Flame stability is affected by fuel moisture content [Shanmukharadhya. and Sudhakar 2007] and the volatiles content of the fuel [Silvia *et al.* 2008]. High fuel moisture content makes de-volatilisation slower allowing the fuel to mix and react more efficiently in the bed leading to reduced CO emissions [Fryda *et al.* 2006]. High moisture in biomass can also lead to higher NO emissions [Suksankraisorn *et al.* 2003]. Higher moisture content fuels require a higher fuel mass flow rate. The evaporated water vapour also causes increased fluidisation velocities [Fryda *et al.* 2006]. However, if the moisture content is too high it can lead to de-fluidisation of the bed material and also reduce bed temperatures below levels that are too low to sustain

the combustion process. Wu, *et al.* (1999) found that a high moisture content of the fuel, (60%) caused excessive swings in bed temperature so that the fuel was partially dried to a moisture level of 20 – 30% to ensure stable combustion.

High moisture content fuels can also be in the form of a liquid and in this case the liquid feed should be uniformly distributed on the fluidised solid bed particles. The liquid feed should contact the largest possible amount of the bed solids by forming a thin liquid film on the solid particles [Grey, 1994]. Atomisation leading to finer liquid droplets can also enhance the liquid-solid contact within the fluidised bed [Portoghese, *et al.* 2007].

The combustion efficiency is also affected by the moisture content of the fuel and when based on the Lower Heating Value (LHV) of the fuel typical combustion efficiency ranges from 65% in poorly designed furnaces to 99% in well insulated sophisticated combustion systems [Peter *et al*, 1999]. The LHV is affected by moisture content in two ways. Firstly, high moisture content means a lower content of combustible material per kg of fuel. Secondly, higher energy is required to evaporate the moisture in the fuel. In practice the maximum allowable moisture content of a fuel on a wet basis should not be above about 55% to extract energy from it by combustion [Peter *et al.* 1999].

Yang *et al.* (2003) investigated the incineration of simulated solid waste consisting of cardboard and potatoes and biomass (pinewood) at different moisture levels ranging from 7.5% to 47% in a fixed bed reactor. Ignition was provided by a gas burner at the top of the chamber. They observed that when all the moisture in the fuel is evaporated the bed temperature rises quickly because further heat is not needed to evaporate the moisture and the sharp increase in the release of volatiles produces large amounts of CO.

Yang *et al.* (2003) investigated the behaviour of the fixed-bed at different fuel moisture contents and found that the time for the bed-top temperature to begin to pick up sharply was much longer at 45% moisture than that at 30% moisture. The higher moisture content prolonged ignition of the bed so that at 30% moisture the temperature rose rapidly but at 45% moisture it took longer. They observed unstable combustion conditions at 45% moisture in the middle of the combustion process. They also found that the moisture evaporation and

volatile release rates were lower for 45% moisture than that for 30% moisture and char burning rate was higher for 45% moisture than that for 30% moisture.

At 47% moisture the local peak temperature was lower than at 30% and 45% moisture. At 47% moisture they found that the flame temperature dropped to an unsustainably low level of 200 °C in the middle of the combustion process and that the flame was virtually extinct. They found that the average burning rate in the bed decreases non-linearly with the increase in the moisture content of the fuel. It was observed that for drier fuels combustion was sub-stoichiometric because the volatiles release was faster and a large amount of unburned gases exited from the top.

2.6 Meat Industry wastes:

Waste from the poultry industry includes a blend of excreta (manure), bedding material, chicken litter (CL), waste feed, dead birds, broken eggs and feathers. Poultry litter can have a moisture content of up to 43% [Abelha *et al.* 2003]. The high moisture and ash and low CV of poultry litter causes problems in maintaining steady and complete combustion [Kelleher *et al.* 2002; Sweeten *et al.* 2003]. The calorific value of poultry litter decreases with increasing moisture content. Dried samples have a typical CV of 13.5 MJ/kg almost half of that of coal [Abelha *et al.* 2003]. The ash of poultry litter contains high Ca, K and Na and low Si indicating that the ash fusion temperature is relatively lower and Sulphur retention ability is relatively high as compared to coal [Li *et al.* 2008].

Meat and bone meal (MBM) is produced in rendering plants where animal offal and bones are mixed, crushed and cooked together. During this process, tallow is extracted and the remaining material which is dried and crushed further is known as MBM [Bradley, 1991]. MBM is a granular and sticky material containing fragments of bones, characterised by high volatile and ash contents and rich in calcium (Ca), phosphorus (P), Cl and alkali (Na) [Fryda *et al.* 2007]. MBM has an average calorific value of 16.18 MJ/kg [Power Gen, 1997] and a bulk density of 700 kg/m^3 [McDonnell, 2001]. It has been shown that co-firing of milled MBM (2 mm) with coal in pulverized coal boilers (with thermal outputs of 0.5 MW and 1 MW) is possible [Power Gen, 1997; National Power Technologies, 1997]. Proximate and ash analyses of poultry litter and MBM are given in Tables 2.1 and 2.2, respectively.

2.6.1 Combustion of Meat Industry wastes:

One of the disposal methods for poultry wastes is direct combustion which has the potential to provide a cost effective environmentally benign disposal solution for the litter. It can be used to provide energy for both space heating of poultry houses and large scale schemes involving power generation or combined heat and power [Li *et al* 2008]. Nevertheless there remain technical and operational challenges associated with the processing of poultry wastes due to the inherent variability of the waste stream [Florin *et al.* 2009].

Florin *et al.* (2009) identified and examined the opportunities and risks when burning poultry waste from Australian poultry farms. They characterised typical poultry waste streams based on composition, and undertook thermodynamic equilibrium modelling using FactSage, a commercial equilibrium modelling package. They assumed a feedstock composition of 20% moisture, 55% volatiles and 25% ash. The materials used for analysis contained manure (moisture 12.9 – 24.4%) and litter (moisture content 18.1%). They concluded that under current legislation in Australia the land application of untreated waste is the most suitable method of application.

Agglomeration and clinkering of fluidised beds can be a problem with biomass fuels so that Ohman *et al.* (2003) determined the characteristics and critical bed agglomeration temperatures of MBM, refuse derived fuel (RDF) and blends of these during combustion in a 5kW bench scale fluidised bed combustor. Meat and bone meal (47% meat) and RDF were combusted with dolomite and kaolin as bed additives. They conducted controlled agglomeration tests by operating the bed with 6% O_2 and four times the minimum fluidising velocity.The bed temperature was maintained at 730 °C for all the fuels tested to avoid agglomeration. At an ash amount corresponding to a theoretical value of about 20 wt % ash in the bed, the fuel feeding was stopped and the operation was switched to external heating. The bed was then heated at a rate of 3 °C/min until a critical agglomeration temperature was reached. They found that the agglomeration temperature with MBM alone was 805 °C. With the addition of RDF (2/3 on an energy basis) it went up to 830 °C. Addition of 5% dolomite to the MBM/RDF blend took the agglomeration temperature to 860 – 890 °C while the addition of 5% kaolin resulted in agglomeration at 905 °C. They concluded that MBM

combustion in fluidised beds with quartz as the bed material is problematic and addition of kaolin and possibly dolomite could reduce the risk to moderate levels.

Table 2.1: Proximate and ultimate analysis of poultry litter and MBM

Proximate and ultimate analysis	Poultry litter [Henihan *et al.* 2003]	MBM [Fryda *et al.* 2007]
Fixed Carbon (%)	1.66	8.61
Volatiles (%)	38.91	79.7
Ash (%)	16.42	10.4
Moisture (%)	43.01	1.35
C (%)	39.57	55.7
H (%)	5.11	8.03
O (%)	48.27	18.58
N (%)	5.31	7.15
S (%)	0.77	0.05
HHV (MJ/kg)	10.62	30.29

Table 2.2: Ash analysis of MBM weight % of Fuel

Compound	MBM [Fryda *et al.* 2007]	Element	Poultry litter [Abelha *et al.* 2003]
SiO_2 (%)	5.97	Ca	1.5%
Al_2O_3 (%)	1.81	K	3.1%
TiO_2 (%)	0.11	Fe	0.1%
Fe_2O_3 (%)	0.59	Mn	596 µg/g
CaO (%)	45.6	Zn	209 µg/g
MgO (%)	1.43	Cu	71 µg/g
Na_2O (%)	2.07	Cr	112 µg/g
K_2O (%)	1.86	Ni	<LL (LL=10 µg/g)
P_2O_5 (%)	37.3		

Senneca (2008) studied the kinetics of char combustion for MBM. They carried out co-firing of 6% MBM (moisture content 6%) with 94% coal in a 165 MW_e pulverized fuel boiler and ash samples were collected and compared with ash samples with coal alone firing collected from the same locations. They found that at low temperatures MBM has a high combustion rate compared to most other fuels even two orders of magnitude higher than coal. At higher temperature the rate becomes lower than that of other biomass and is comparable with that of coal. This was attributed to the high mineral matter of MBM which undergoes transformations at high temperature and combustion reactivity is depressed.

2.6.2 Co-combustion of Meat Industry wastes:

A number of experimental studies concerned with co-firing of meat industry wastes such as poultry litter and MBM have been undertaken and some of the most relevant work is described in this section.

McDonnell, (2001) manually dropped pellets, made by mixing MBM (from poultry and fish) and peat, into a 10 cm diameter fluidised bed combustor in order to determine their combustion stability. Alumina oxide was used as the bed material. Bed temperature was kept at 880 °C and superficial gas velocity was 0.8 m/s. They found that the peat-MBM pellets displayed volatile combustion for a mean period of between 40 and 50 sec. The residence time for combustion of the MBM was increased when mixed with peat and the compaction pressure was increased. Reducing the proportion of MBM resulted in less volatile behaviour as demonstrated by reductions in flame height and intensity. The longest char combustion periods, an average of 387 sec, were observed with peat pellets as compared with 64 sec for 100% MBM. It was concluded that the maximum MBM proportion in the pellets appears to be about 35% since higher rates than this produce soft pellets which have a higher risk of break up and disintegration during the combustion phase in the fluidised bed.

Fryda *et al.* (2006; 2007) co-fired MBM (moisture content 1.35%) in a laboratory scale fluidised bed combustor with two coals, a high rank Colombian coal (moisture content 4.2%) and a low rank Greek lignite (moisture content 24.32%) and olive oil bagasse (moisture content 8.5%). They determined the effect of different fuel blends on the emissions and agglomeration tendency and reported feeding and agglomeration problems with MBM.

During the co-combustion experiments of dry olive bagasse-Meat Bone Meal (MBM) soon after the initiation of combustion, loss of fluidisation occurred in all cases and practically no steady state conditions were reached. However co-firing of MBM with the coals was successful and they found that in the lignite blends combustion efficiency was around 99% while in the case of Columbian blends it was 87 – 90%.

Figure 2.1 shows CO emissions from the combustion of pure lignite and Colombian coal with MBM as a function of excess air for different coal-MBM blends. It can be observed from the figure that pure lignite combustion has low CO emissions than Colombian coal combustion which has higher CO emissions. The effect is more pronounced at lower fluidisation velocities. The 100% Greek lignite combustion is more efficient compared to 100% Colombian coal because of lower volatiles and higher moisture content making devolatilisation step slower and allowing the fuel to mix more efficiently, leading to reduced CO emissions. The results of SO_2 and NO_x emissions observed by Fryda *et al.* are given in the in Chapter 6 and agglomeration problems observed by them are discussed later in this Thesis, in Chapter 7.

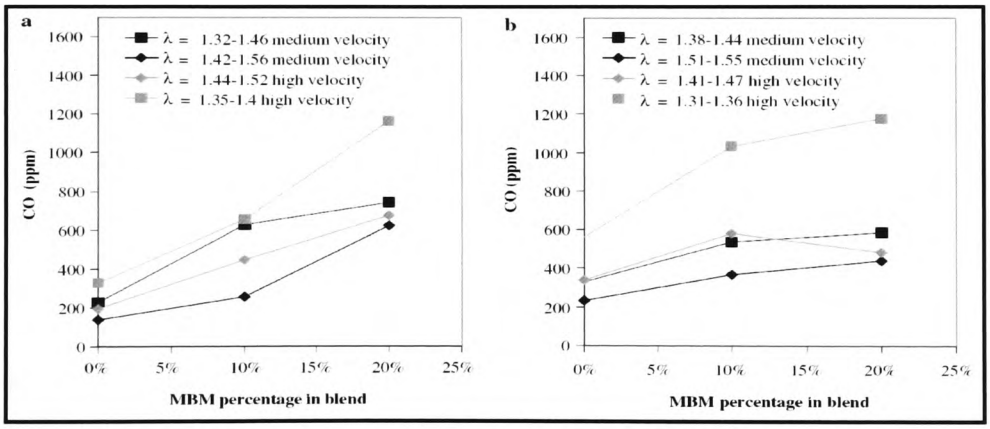


Figure 2.1: CO emissions from lignite (a) and Colombian coal (b) blends with MBM(corrected to 6% O_2) [Fryda *et al.* 2006]

Abelha *et al.* (2003) combusted 100 % poultry litter (moisture content of up to 43%) and co-combusted 50% of this poultry litter with peat (moisture content 24.1%) in an atmospheric bubbling fluidised bed combustor of square cross section 300*300 mm and 5000 mm high. They investigated the effect of moisture content, air staging and variation in excess air levels

along the freeboard. The bed was maintained at about 800 °C, a temperature high enough for rapid de-volatilisation and stable combustion. They varied excess air from 10 – 15% and fluidising velocity between 0.4 – 0.5 m/s to give sufficient residence time of 2 sec at a temperature of 850 °C. They found that as long as the moisture content of the poultry litter was kept below 25%, peat was not needed for stable combustion.

They found that during co-combustion with peat, due to the high moisture content of the poultry litter careful control was also needed to have a stable and sustainable operation. Air staging improved the combustion efficiency as measured by CO emissions and lowered NO_x emissions, see Table 2.3. It can be observed from the table that for 100% poultry litter the CO emissions (corrected to 11% O_2) were decreased from 1500 – 6000ppm to 360 – 540ppm when secondary air was used and were decreased to 50 – 120ppm when secondary air was split in two stages. Similarly NO_x emissions (corrected to 11% O_2) were decreased from 280 – 360ppm to 160 – 180ppm when secondary air was used and were decreased to 120 – 140ppm when secondary air was split in two stages. However, with 50/50 peat-poultry litter blend CO emissions were increased from 50 – 120ppm to 180 – 300ppm while NO_x emissions decreased from 120 – 140ppm to 80 – 120ppm when secondary air was split into two levels. They also reported a major problem to be the feeding of poultry litter into the bed due to its high moisture. Even the presence of peat did not improve the flow characteristics of the litter if the moisture content of the blend was above 22%. This problem with smooth flow was also observed by Annamalai *et al.* (1985) who had to dry MBM to a moisture content of 11%.

Poultry litter has a relatively high content of potassium, mainly due to the presence of straw. The potassium content can result in bed agglomeration due to the formation of low melting point alkali metal eutectics if the bed temperature is increased above 800 °C. However no agglomeration was observed by Abelha *et al.* (2003) possibly because the bed was shallow (200 – 320 mm) and was well fluidised preventing the formation of agglomerates. The bed temperature was also controlled to release Potassium (K) in the form of volatiles so that most of the potassium was entrained in the gases and collected in the cyclones. Clark (1993) and Barton *et al.* (1990) found that at combustion temperatures above 800 °C, most of the heavy metals vaporised and passed to the gas phase.

Table 2.3: Variations in CO and NO_x concentrations with air staging [Abelha *et al.* 2003].

	CO concentration (ppm, 11% O_2)	NO_x concentration (ppm, 11% O_2)
100% poultry litter with no secondary air	1500 – 6000	280 – 360
100% poultry litter with secondary air		
Secondary air/fluidising air = 0.4 No staging Little turbulence	360 – 540	160 – 180
Secondary air/fluidising air = 0.4 Two-level staging Strong turbulence	50 – 120	120 – 140
50% poultry litter and 50% peat with secondary air		
Secondary air/fluidising air = 0.4 Two-level staging Strong turbulence	180 – 300	80 – 120

Ignition temperature is a function of fuel moisture content. Annamalai *et al* (1985) determined the ignition temperature of the 11% moisture content MBM to be 580 °C. For 20% moisture content MBM, Abelha *et al.* (2003) found that the temperature had to be over 620 °C to initiate combustion and moreover these authors found that poultry litter has a low ash fusion temperature of 932 K (659 °C).

Henihan *et al.* (2003) studied the co-firing of a blend of 50/50 (wt%) peat and poultry litter in a fluidised bed combustor of square cross section 300*300 mm and 5m high. Typical moisture content of the poultry litter was 43% and that of peat was 24.1% whilst the corresponding GCVs were 10.6 MJ/kg (poultry litter) and 21.26 MJ/kg (peat). Bed temperatures were varied between 750 – 850 °C with freeboard temperatures from 830 – 950 °C, the average poultry litter particle size was 1 mm while that of peat was 2.5 mm, and the excess air in the bed was 5 – 12%. The fluidised bed was the same as that used by Abelha *et al.* (2003) at INETI in Portugal. They have shown that CO, VOC_s and NO_x emissions can be

reduced to below 200, 25 and 120ppm (corrected to 11% O_2) respectively by adjusting the ratio of secondary air to fluidising air to 0.4 and feeding the secondary air in stages. Without secondary air nitrogen to NO_x conversion was 30% which decreased to 15 – 18% when secondary air was used in stages. Emissions of SO_2 were found to be very low, of the order of 4 and 6 ppm due to low sulphur content of both peat and poultry litter as well as formation of $CaSO_4$ due to the presence of Ca in ash. Again Henihan *et al.* demonstrated that co-combustion of poultry litter and peat is not only possible but also that the emissions are not hazardous. However, they have not described the effect of variations in operational parameters such as feed rate, excess air etc. on efficiency and emissions.

The emissions data obtained by Henihan *et al.* (2003) was used for dispersion modelling of the pollutants, NO_x, CO and SO_2, and pollution levels for a proposed full scale, practical site and it was concluded that ground level concentrations for emissions data would be below the limits and guidelines set by air quality standards.

Li *et al.* (2008) burned different proportions by mass (0% , 10%, 25%, 50%) of poultry litter (moisture content 11.3%) with high sulphur, high chlorine bituminous coal in an atmospheric fluidised bed combustor of 76 mm ID and 1.2 m high. Poultry litter they used had a high oxygen content of 35%. They investigated the effect of poultry litter proportion on pollutant emissions; however, they have not given any information on the combustion efficiency.

They found that CO emissions increase with increases in the mass fraction of poultry litter in the fuel. This is due to high amounts of volatiles released from the litter which are a source of CO and also the presence of these volatiles subsequently inhibit the oxidation of the CO. Furthermore, the high levels of volatiles in poultry litter (57.8%) can create a strongly reducing atmosphere above the bed that inhibits the oxidation of H_2S to SO_2 so that conversion of S to SO_2 decrease with an increasing proportion of Chicken Litter in the blend see, Figure 2.2A. They found that increasing poultry litter proportion in the fuel from 10% to 25% increased the NO emissions slightly, from around 412ppm to 418ppm, as a result of the higher N content of poultry litter (3.4%) compared with that of the coal (1.4%). However, when proportion of poultry litter was increased even further to 50%, the NO emissions decreased to around 368ppm, see Figure 2.2B. They concluded that probably at the lower proportions of poultry litter the release of volatile matter does not result in the presence of

reducing atmospheres which suppress the formation of NO_x. At 50% poultry litter the volatiles concentration is high enough to create a fuel rich atmosphere in the freeboard which reduces the rate of formation of NO_x.

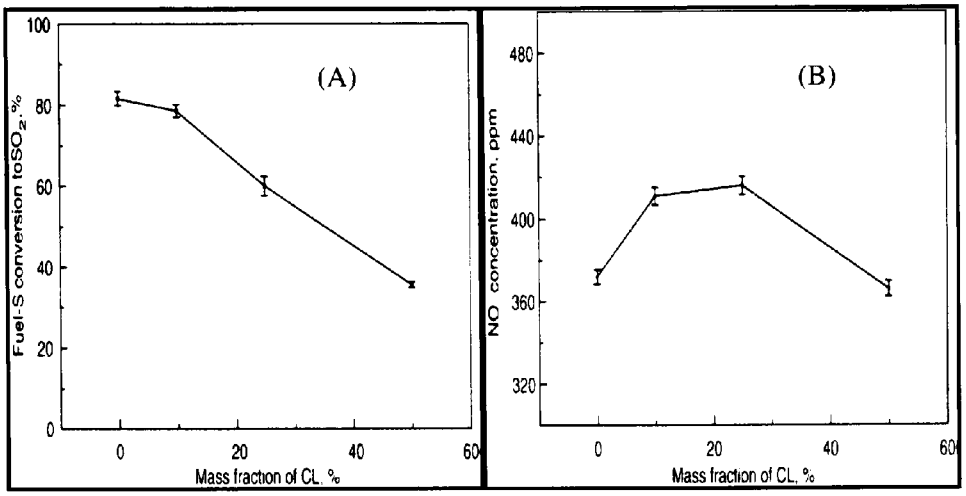


Figure 2.2: SO_2 and NO emissions as a function of poultry litter (CL) mass fraction

Gulyurtlu, *et al.* (2005) carried out combustion tests on the pilot scale fluidised bed combustor installed at INETI, using different proportions by mass 0, 20, 50 and 100% of MBM, produced in Portugal and having a moisture content of 6.8%, mixed with a Colombian 'El Cerejon' coal. The combustion air was split between fluidising air and secondary air and the fuel feed was introduced at 0.5 m above the distributor plate. The secondary air was introduced at two different levels 1.1 and 2.1 m above the distributor plate. They monitored gaseous emissions and the results they obtained are summarised in Table 2.4. They observed increase in SO_2 emissions with increase in the amount of coal in blends from 14 mg/Nm^3 (100% MBM) to 713 mg/Nm^3 (0% MBM) due to higher S content of the coal (0.7%) than the MBM (0.5%). Percentage of inlet Sulphur conversion to SO_2 was found to be 2, 28, 39 and 50% with decreasing the MBM proportion from 100 to 0%. Fuel N conversion to NO_x was found to decrease from 9.6 to 1.4% with increase in the MBM proportion although nitrogen content of the MBM (8.4%) is about eight times higher than that of the coal (1.5%). A 20% (wt%) MBM addition to the fuel resulted in the reduction of NO_x by 25% as compared to the combustion of coal alone, although the nitrogen input was almost double. They observed that NO_x emissions did not go up as expected with increase in MBM fraction in the fuel even at higher amounts of secondary air used to burn volatiles. It could be due to the reason that the

burning of volatiles above the bed resulted in higher temperature of 1000 °C which is favourable for NO_x reduction by $DeNO_x$ mechanism.

Gulyurtlu, *et al.* (2005) also characterised the ashes collected from the bed, cyclone and stack by measuring their composition, leachability, eco-toxicity and presence of unburned proteins. They found that sulphur content in the first cyclone ash decreased from 0.97 to 0.66% and in the second cyclone ash varied from 2.77% to 0.63% with increase in coal fraction in the fuel although the sulphur content of the coal was higher than MBM, see Figure 2.3. Similar trend was observed in the bed ash and was attributed to the presence of Ca which tends to capture sulphur.

Gulyurtlu, *et al.* (2005) observed that with 100% MBM firing the bed tends to agglomerate and de-fluidise at 820 °C whilst below this temperature no agglomeration problems were observed. They also observed substantial burning of MBM in the freeboard as the freeboard temperature reached about 1000 °C. The increase in this temperature was lower with reduced amounts of MBM in the fuel blend due to relatively lower amount of volatiles introduced.

Table 2.4: Operating conditions and gas emissions for MBM-Coal blends*

Concentration	Fuel composition			
	100% MBM	50% MBM	20% MBM	100% Coal
	Operating conditions			
Bed temperature (°C)	730	770	770	850
Freeboard temp. (°C)	760 – 1000	660 – 880	560 – 840	540 – 850
Fuel flow (kg/h)	16.5	11.7	10.5	9.8
Excess air (%)	93	67	56	50
Secondary air (%)	42	28	21	18
	Emissions			
CO	8	165	281	270
N_2O	37	115	139	86
NO_x	398	273	201	259
SO_2	14	321	502	713

* (mg/Nm^3, 11% O_2) [Gulyurtlu, *et al.* 2005]

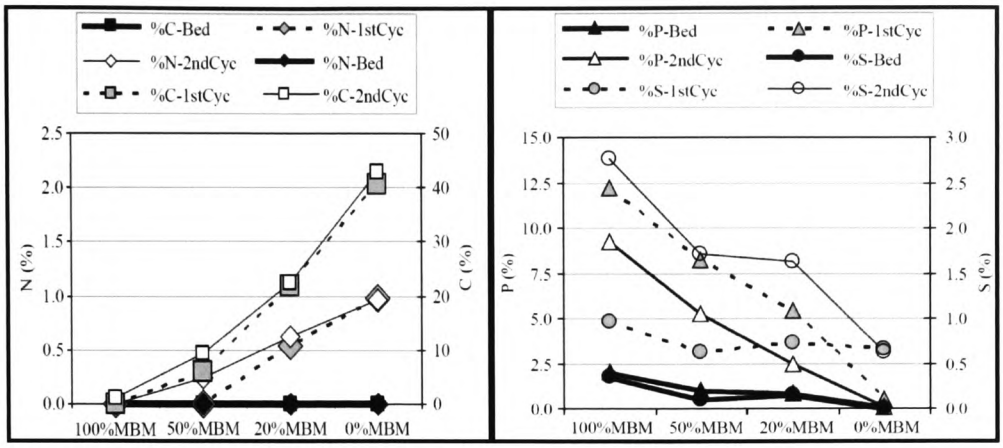


Figure 2.3: Nitrogen, carbon, phosphous and sulphur content in bed and cyclone ashes[Gulyurtlu, *et al.* 2005]

The above review concludes that due to high moisture content feeding of MBM is a problem and need to be dried. Also, blending of MBM with coal can improve its flow properties. Co-firing of MBM with lignite and coal in fluidised beds is feasible with combustion efficiencies as high as 99%. However, co-firing of MBM with dry olive bagasse is problematic and causes de-fluidisation of the bed due to low ash fusion temperature of MBM. Poultry litter can sustain combustion on its own up to a moisture content of 25%. Above this moisture support fuel such as coal is needed for sustained combustion process. Due to the high moisture content of the poultry litter careful control is needed for a stable and sustainable operation. Introduction of secondary air decreases CO and NO_x emissions when pure poultry litter is combusted and the emissions further decrease when secondary air is split in two stages. However, when co-firing with peat CO emissions increase while NO_x emissions decrease when secondary air is used in stages. During co-firing, emissions of CO and SO_2 decrease while those of NO first increase and then decrease, with increase in the proportion of poultry litter in the blend.

2.7 Industrial Sludge:

Industrial sludges are other materials with a high moisture content which have been co-fired with coal so that these are briefly reviewed. Industrial sludges have a variety of different origins and thus different compositions and properties. An example of the analysis of sludge from olive oil industry is given in Table 2.5 from [Armesto, *et al.* 2003]. A major source of

sludge is that originating in paper mills. Since every tonne of recovered fibre creates 200 to 400 kg of sludge (dry weight) [Wiktorian Tarnawski, 2004] land filling is not a suitable solution from the environmental point of view, so that thermal treatment is appropriate [Oral *et al.* 2005].

An other important sludge is that originating from the olive industry which contains olive husk which in turn consists of pulp, olive stones, residual oil and 50 – 55% water [Celam *et al.* 2008]. Dry olive husk, which is sold as a fuel for small boilers, has a heating value of 18 – 22 MJ/kg [Arvelakis and Koukios, 2002; Jenkins *et al.* 1998].

Sludges are of low CV due to their high moisture and ash contents. The wet sludge after dewatering from paper mills (65 – 84% moisture) is very soft and behaves like a paste and has lower heating value ranges from 0.7 to 1.8 MJ/kg [Oral *et al.* 2005] which is unsuitable for sustainable combustion on its own. Therefore, the sludge must be dried before combustion or an auxiliary fuel needs to be used to assist combustion.

Table 2.5: Analysis of Sludge from olive oil industry [Armesto, *et al.* 2003]

Proximate and Ultimate analysis		Composition of Ash	
Fixed Carbon (%), db	19.7	SiO_2 (%)	21.2
Volatiles (%), db	74.5	Al_2O_3 (%)	2.9
Ash (%), db	5.8	TiO_2 (%)	0
Moisture (%)	66.4	Fe_2O_3 (%)	2.7
C (%), db	52.2	CaO (%)	13.8
H (%), db	6.7	MgO (%)	8.4
O (%), db	34	Na_2O (%)	0.5
N (%), db	1.1	K_2O (%)	42.5
S (%), db	0.1	P_2O_5 (%)	5.5
Cl (%), db	0.3	MnO	0.1
LHV (MJ/kg), raw	6.6	Others	2.4

2.7.1 Combustion and Co-Combustion of Sludge:

Industrially, many solid wastes can be classified as biomass and their usage reduces disposal costs [Silvia *et al.* 2008]. One of the main limitations of the use of biomass residues as energy source is their availability and moderate heating power which leads to small scales and high costs as compared to fossil fuels [Celam *et al.* 2008]. Waste fuels like water treatment sludges (63% moisture), de-inking sludges (58% moisture) and black liquor (blend of lye and organic substances removed from wood chips) are all burned in BFB or CFB boilers. A comparison of the advantages and disadvantages of sludge incineration for converting waste to energy with those of disposal by land filling leads to the conclusion that the thermal treatment of sludge by a suitable technology is a favourable option both economically and environmentally [Oral *et al.* 2005]. The best combustion results and controllability is achieved when fuel moisture does not exceed 60% [Wiktorian Tarnawski, 2004].

Silvia *et al.* (2008) characterised seven wastes from the textile and food industries (including textile residues, coffee grounds, orange waste and meat industry waste water sludges) and measured emissions as a result of burning three of them (textile residues, coffee grounds and blend of sludge and saw dust) in a pilot cyclone type combustor with capacity of 100 kg/h. The LHV of the wastes ranged from 14.22 to 22.93 MJ/kg and they were all dried in an industrial rotating granulator before combustion. They also investigated the effect of recirculation of flue gas on emissions. Meat processing sludge and saw dust blend (1:9 by mass) was burned (50.23% moisture) at 900 °C at a feed rate of 95 kg/h. The operating conditions they used during combustion tests and results of the emissions (corrected to 7% O_2) are summarised in Table 2.6. Comparison of textile residue combustion tests show that with increase in recirculation rate emissions of CO increased while those of NO_x, SO_2 and C_xH_y decreased, see Table 2.6. Typical emissions for mix of meat sludge and sawdust waste corrected to 7% O_2 were found to be, CO 735 mg/Nm^3, NO_x 498 mg/Nm^3 and SO_2 129 mg/Nm^3. The data shows that the emissions of NO_x and SO_2 for the meat sludge and sawdust waste are the lowest while those of CO and C_xH_y are the highest.

Ash from the sludge and sawdust waste starts to melt at 1335 °C which is well above the typical operating bed temperatures of fluidised beds and thus would not be of concern, see

Table 2.7, which shows the ash melting behaviour of this blend and textile residues compared with that of coal from Bryant, *et al.* (2000).

Silvia *et al.* used thermo gravimetric analysis to investigate carbon reactivity of these materials. They found that volatile matter release represents the maximum mass loss rate an important parameter to adjust combustion chemistry. They observed that the sludge and sawdust waste blend presented the lowest while the textile residue represented the highest mass loss rate of the three wastes tested. Ignition and peak temperature of the wastes tested were similar and they found that the ignition and peak temperatures of the mix of meat sludge and sawdust waste were found to be 185 °C and 348 °C, respectively. For textile residues and coffee grounds the temperatures were found to be 223 °C and 179 °C (ignition) and 325 °C and 323 °C (peak), respectively.

Table 2.6: Operating conditions and Emissions from Textile residue, Coffee grounds and blend of Sludge and sawdust[Silvia, *et al.* 2008]

	Textile residue1	Textile residue2	Coffee grounds	Sludge and sawdust (1:9)
Fuel feed rate (kg/h)	100	95	85	95
Combustor Temperature (°C)	1228	1200	1219	900
Gas recirculation (%)	25	50	50	0
CO (mg/Nm^3)	27.65	52.73	126.6	734.83
NO_x (mg/Nm^3)	1204.60	1007.84	1663.28	497.94
SO_2 (mg/Nm^3)	1747.67	1415.08	141.92	128.69
C_xH_y (mg/Nm^3)	11.52	<0.01	<0.01	554.44

Table 2.7: Ash melting behaviour of Coal and blend of Meat and Sawdust [Silvia *et al.* 2008]

	Meat sludge and sawdust waste	Textile residues	Coal [Bryant, *et al.* 2000]
Deformation temperature °C	1335	950	1270
Softening temperature °C	1359	>1500	1510
Hemispherical temperature °C	1361	>1500	1530
Fluid temperature °C	1364	>1500	1550

Oral *et al.* (2005) combusted dewatered sludge in a fluidised bed combustor. The sludge moved counter flow to the flue gas and thus was pre-dried before entering into the fluidised bed. When built the unit was modern and up-to-date but with more and more sweeping environmental laws the plant needed retrofit due to higher than allowable emissions of particulates (due to rather low efficiency of flue gas cleaning system), CO and C_xH_y (due to unsuitable process arrangements in the incineration unit). In order to improve the performance, the system was retrofitted. The combustion chamber was supplemented by an afterburner to ensure the combustion of CO and hydrocarbons. The combustor was provided with flue gas by-pass to efficiently control flue gas volume through hearths, and thus temperature. The scrubber was modified and a liquid droplet separator and a particulate solid separator were incorporated. Original bulk conveyor for sludge transport was replaced with high pressure volumetric pump. Performance of the combustor was significantly improved after modifications. The performance of the unit before and after retrofit is summarized in Table 2.8 and indicates how CO, hydrocarbon and solid particulate emissions can be reduced. This indicates that proper design and operation of the fluidised bed is necessary to achieve satisfactory combustion of these high moisture sludges.

Table 2.8: Performance of FBC on sludge [Oral *et al.* 2005]

Pollutant	Measured (mg/Nm^3)		Allowable (mg/Nm^3)
	Before retrofit	After retrofit	
NO_x	50 – 227	200 – 250	350
CO	2200 – 3100	20	100
C_xH_y	<100	0	20
Solid particles	100 – 157	20 – 25	30

Patumsawad and Cliffe, (2002) demonstrated the technical feasibility of fluidised bed combustion as a clean technology for burning high moisture simulated MSW and other wastes. Pre-dried chicken manure pellets were selected as the simulated MSW. The pellets have a moisture content of 5% and are cylindrical in shape with an average diameter of 2 mm and length of 10 mm. Water was added to the sample to generate the required percentage of moisture content. They investigated firing and co-firing of high moisture MSW, vegetable waste and olive waste with coal, over a range of different moisture contents. The moisture contents of the wastes they studied for combustion were 5%, 10%, 15% and 20 %. Co-firing of 60% moisture content in simulated MSW with coal, vegetable waste with coal and olive oil waste with coal was also investigated. For the co-firing tests, the excess air was 40 and 60%, bed temperature was between 850 – 900 °C and fractions of waste were 0, 10, 15 and 20%. They found the maximum moisture content of the simulated MSW that could be burnt was 20%. At higher moisture content the bed temperature was below 600 °C so that stable combustion could not be maintained. They found that the combustion efficiency was decreased when co-firing the wastes as compared to coal alone.When 60% moisture content simulated MSW at 10%, 15% and 20% concentration by mass was co-fired with coal they found that the combustion efficiency decreased by almost 12% compared to burning 100% coal (80% and 92%, respectively), see Figure 2.4. The combustion efficiency of co-firing vegetable waste and olive oil waste with coal were similar to that of coal.

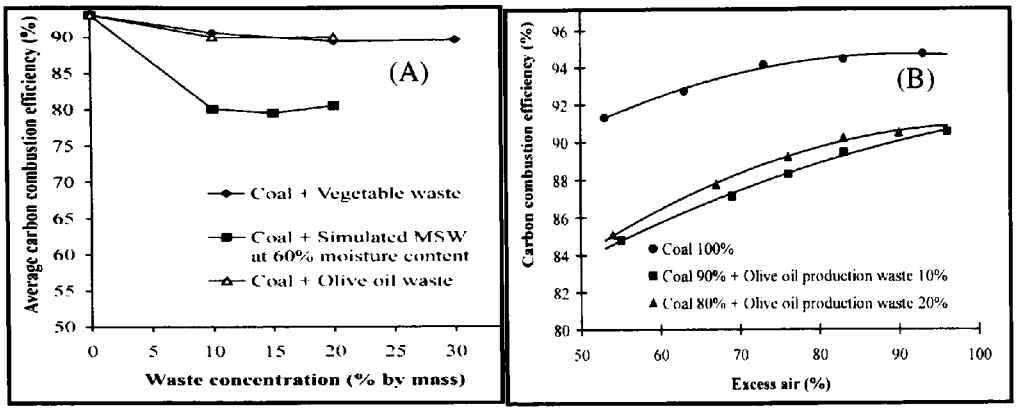


Figure 2.4: Effect of waste concentration and excess air on combustion efficiency A) [Patumsawad and Cliffe, 2002]; B) [Cliffe and Patumsawad, 2001]

They also found that effect of changes in ash content was more pronounced than that of moisture content when comparing combustion efficiency of blends of simulated MSW and coal with those of vegetable waste and coal. Higher the ash content of the fuel, the lower the combustion efficiency due to elutriation of unburned char. Keeping the moisture content constant, they found that average combustion efficiency was 80% for co-combustion of simulated MSW-coal (ash content 26%) and 90% for coal-vegetable waste (ash content 5%), respectively. They also found that increasing moisture content caused simulated MSW particles to stick together so that feeding of the fuel was difficult. The combustion efficiency when co-firing simulated MSW decreased with increasing moisture content so that the highest value of 70% occurred with 10% moisture.

Dong *et al.* (2002) co-fired MSW (from Nanjing, China) and coal (Xuzhou, Bituminous) in a 0.2 MW_{th} CFB and studied emissions of NO, N_2O, HCl and SO_2. They found that temperature in the dilute region was 100 – 300 °C higher than that with coal only firing due to combustion of volatiles in the dilute region. The emissions data they obtained is given in the next section on emissions.

2.8 Emissions:

Combustion of biomass has an effect on the emissions so that it is relevant to review this aspect. The combustion of fossil fuels in stationary and transport systems is the main source

of air pollution also called anthropogenic pollution [Basu, 2006]. It is desirable to reduce these emissions due to environmental concerns. However it is not always easy as if some of the combustion parameters are adjusted to decrease emissions of one gas component emissions of other gases may increase.

Emissions from large combustion plants >50 MWth in the EU are limited by Council Directive 88/609/EEC of 1988 [EC, 2006] later replaced by Directive 2001/80/EC.The large combustion plants directive (LCPD) is concerned with the major pollutants SO_2, NO_x and particulates [Brian, 2002]. When burning wastes the emission limits are based on the Waste Incineration Directive as given in Table 2.9.

The main pollutants emitted by combustion systems are discussed in brief in the following paragraphs.

Table 2.9: Waste Incineration Directive Air Emission limit values (273 K, 101.3 kpa, 11%O_2, dry) [Brian, 2002]

	Daily average	Half hourly average (100%)
Total dust (mg/Nm^3)	10	30
Total organic carbon (mg/Nm^3)	10	20
Hydrogen chloride (HCl) (mg/Nm^3)	10	60
Hydrogen fluoride (HF) (mg/Nm^3)	1	4
Sulphur dioxide (mg/Nm^3)	50	200
Nitrogen oxides (mg/Nm^3)	200	400
Carbon monoxide (mg/Nm^3)	50	100

2.8.1 Carbon Monoxide (CO) Emissions:

CO emissions are caused by incomplete combustion of the fuel. High volatile fuels can lead to higher CO emissions due to high hydrocarbon concentration in the combustion

atmosphere. Emissions of CO for coal combustion fall with increasing air supply to the furnace [Leckner *et al.* 2004]. During co-firing CO emissions decrease with increase in the fraction of secondary fuel (if primary fuel is coal) despite the higher volatile matter content of the secondary fuel. High moisture content of the fuel makes its de-volatilisation slower allowing the fuel to mix and react more efficiently in the bed leading to reduced CO emissions [Fryda, *et al.*, 2006].

An even fuel feed to the furnace is a precondition for low CO emissions [Elmar, 2007]. Bhattacharya and Weizhang (1990) observed higher CO emissions at higher fluidisation velocities and attributed it to shorter residence times. However, Srinivasa Rao (2007) found that CO emissions decrease with increase in fluidisation velocity and he observed that there was no significant change in CO when fluidisation velocity was above 1.1 m/s. Armesto *et al.*, (2002) reported CO emissions in the range of 200 to 2000 mg/Nm^3 and Preto *et al.* (1987) between 250 and 6250 mg/Nm^3 by burning rice husk in a bubbling fluidised bed. Armesto *et al.* (2002) further stated that CO emissions increase with increase in fluidising velocity because of lower residence time as is stated by Bhattacharya and Weizhang (1990). Presence of alkali metal halides increases CO level in the flue gases [Bulewicz and Janicka, 1990]. MSW contains large amounts of Cl and several studies have shown that hydrochloric acid (HCl) formation can inhibit the oxidation of CO. When coal is added to the blend chlorine emissions decrease, the oxidation of CO is favoured, char concentration grows and CO production from char combustion is consequently higher.

Fryda *et al* (2006) compared CO emissions from different fuels with respect to operational parameters. Secondary air is provided above the bed to suppress CO emissions to acceptable legislation limits. They have found that pure lignite has low CO emissions especially for lower fluidisation velocities. Columbian coal has higher CO emissions and are unaffected by velocity. Greek lignite has higher moisture which makes its de-volatilisation step slower allowing the fuel to mix and react more efficiently in the bed leading to reduced CO emissions. CO emissions therefore clearly depend upon the fuel properties and operational conditions.

2.8.2 Sulphur dioxide (SO_2) Emissions:

Sulphur in the fuel is oxidised to SO_2 during combustion process, part of which is subsequently further oxidised to SO_3. In a fluidised bed furnace solids move violently and temperatures in the entire furnace are relatively lower compared with other forms of combustion and are nearly constant. Thus conditions are favourable for the formation of SO_3 and its retention in the ash or additives such as lime stone by forming sulphates. According to Elmer (2007) major portion of the fuel S reacts with sulphates which are kept in the fuel ash.

Due to the reducing environment in the emulsion phase of fluidised beds, carbon monoxide (CO) can dissociate formed calcium sulphate ($CaSO_4$) by the reaction given below [Makarytchev *et al.* 1995; Lyngfelt and Leckner, 1999; Anthony and Granaststein, 2001] and can result in higher SO_2 emissions.

$$CaSO_4(s) + CO(g) \rightarrow CaO(s) + SO_2(g) + CO_2(g) \quad (2.1)$$

Emissions of SO_2 depend upon fuel sulphur content and ash derived CaO that acts as a de-sulphuriser [Fryda *et al.* 2006]. Calcium, potassium or sodium (Na), present in relatively large amounts in biomass fuel ashes, may act as sorbents and may reduce acid gases (HCl and H_2S) emissions [Nordin, 1994 and Nordin, 1995]. Acid gas retention decreases with the increase in coal fraction when co-firing with biomass. With the increase of coal fraction [Desroches-Ducarne, *et el.* 1998] the chlorine and calcium content decreases and S content increases. The Intrinsic molar ratio [Ca/(S+0.5Cl)], decreases and the percentage of captured sulphur or chlorine is lower. The amount of Ca and S present as well as type of Ca compound determines its effectiveness as a de-sulphuriser. For S capture by Ca under fluidised bed conditions both physical and chemical factors are important [Anthony, *et al.* 1998]. The higher the Ca/S ratio of the fuel, the lower the SO_2 emissions [Fryda, *et al.*, 2006]. Replacing coal with biomass having high Ca not only reduces total S but also provides Ca for converting S to $CaSO_4$ in the bed. The presence of alkali halides particularly sodium chloride (NaCl) enhances the extent of S capture by limestone sorbents [Shearer, *et al.* 1970; Smith, *et al.* 1981].

Biomass fuels have lower sulphur contents than coal thus lead to lower SO_2 emissions if co-fired. Suksankraisorn, *et al.*, (2003) reported during co-combustion of coal and MSW that fuel sulphur conversion increases with increase in MSW mass fraction. S to SO_2 conversion increases with the presence of volatiles [Fryda, *et al.*, 2006]. High volatile content in MSW creates strongly reducing conditions which inhibits the capture of sulphur. However, Hein and Bemtgen (1998) observed 75% reductions in SO_2 emissions due to low S in biomass and increased S retention in ash.

Fryda *et al.* (2006) found that with coal-MBM blends, SO_2 emissions are more sensitive to sulphur content than to Ca content, as, Ca in MBM is present as calcium phosphate which is very stable under fluidised bed conditions and is not chemically active as a de-sulphurising agent. They also found that S to SO_2 conversion increases with volatiles as was also observed by Suksankraisorn, *et al.*, (2003) while Ca/S ratio has minor effect. They found that SO_2 emissions were less during the combustion of 10% (wt/wt) MBM-coal, as compared to 20% MBM-coal blend, see Figure 2.5, due to relatively lower volatile increase in the former case. Sulphur to SO_2 conversion was 70 – 80% during tests with 100% Colombian coal and reached up to 90% during tests with 20% MBM-coal blends.

They have not found any detectable SO_2 emissions during the combustion of Greek lignite because of its high CaO content (Ca/S >8). Also emissions of SO_2 from Columbian coal were reduced by the introduction of MBM. They also found that SO_2 emissions were not affected by fluidisation velocity as long as the temperature profile of the bed does not change significantly.

They observed that increase in volatiles caused by MBM plays an important hindering role against de-sulphurisation. Figure 2.6 plots sulphur conversion to SO_2 from the Colombian coal-MBM tests as a function of the volatile charge, i.e. an indicative ratio of the total volatiles concentration expressed as the volatile fuel content input in grams, given in the proximate analysis, per m^3 of theoretically calculated flue gas volume flow. The sulphur to SO_2 conversion increases with volatiles while the Ca/S ratio seems to have a minor effect.

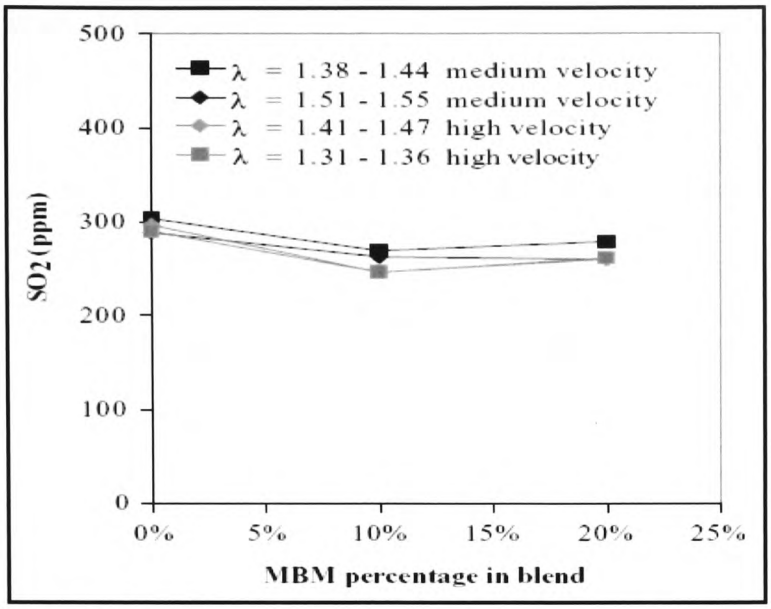


Figure 2.5: SO_2 emissions from Colombian coal co-combustion with MBM under medium and high fluidisation velocities (corrected to 6% O_2) [Fryda *et al.* 2006]

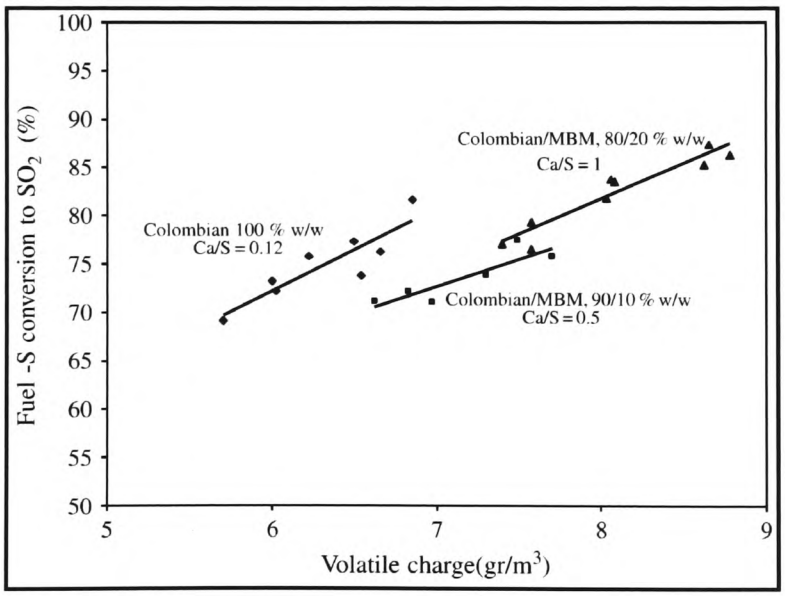


Figure 2.6: Fuel sulphur conversion vs. volatile charge for Colombian coal-MBM blends[Fryda *et al.* 2006]

In a BFB the formation rate of SO_2 increases with temperature, but during co-firing of MSW and coal in a CFB, Dong *et al.* (2002) found that SO_2 emissions remained more or less constant with temperature, see Figure 2.7, due to the higher freeboard temperature and

secondary air supply in this type of fluidised bed. SO_2 emissions were lower at high mixing ratios due to high Ca and low S content of MSW.

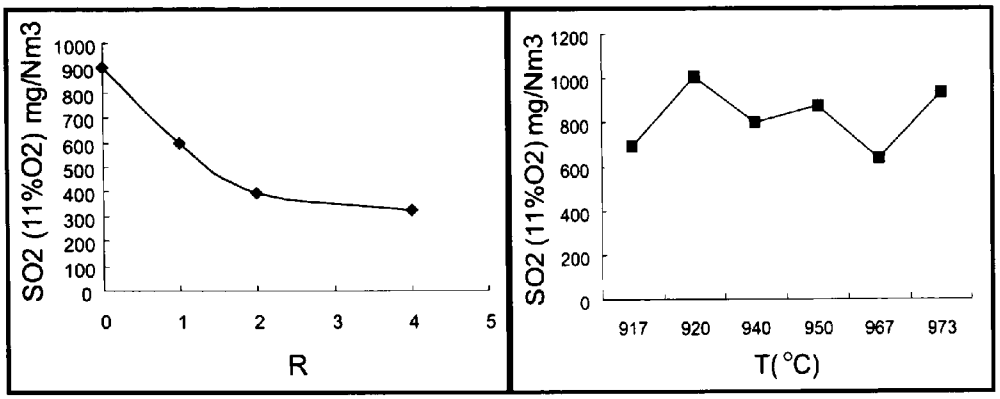


Figure 2.7: Emissions of SO_2 as a function of mixing ratio and temperature [Dong *et al.* 2002]

Above discussion concludes that emissions of SO_2 depend upon fuel sulphur content and ash derived CaO that acts as a de-sulphuriser. Under fluidised bed conditions major portion of the fuel S reacts with sulphates which are kept in the fuel ash. Fuels having higher Ca/S ratio give lower SO_2 emissions. However it also depends upon the type of Ca compounds present, for example, in MBM, Ca is present as calcium phosphate which is very stable under fluidised bed conditions and is not chemically active as a de-sulphurising agent. Biomass fuels have lower sulphur contents than coal thus lead to lower SO_2 emissions if co-fired and acid gas retention decreases with the increase in coal fraction. Calcium, potassium or sodium, present in relatively large amounts in biomass fuel ashes, may act as sorbents and may reduce acid gases, hydrogen chloride (HCl) and hydrogen sulfide (H_2S) emissions. The presence of alkali halides particularly NaCl enhances the extent of S capture by limestone sorbents. Conversion of S to SO_2 increases with the presence of volatiles contributed by biomass due to hindering role of volatiles against de-sulphurisation.

2.8.3 Nitrogen Oxides (NO_x) and Nitrogen Dioxide (N_2O) Emissions:

There is also concern about the emission of the oxides of nitrogen (generically known as NO_x) from combustion processes so that the factors affecting the formation of these pollutants are now briefly reviewed. NO_x emissions can be formed by different ways

including thermal, fuel and prompt mechanisms. Fluidised beds are operated at relatively low temperatures in the range of 850 to 950 °C, thus thermal NO_x (formed at temperatures higher than 1400 °C) is not formed and fuel NO_x dominates. This depends upon the nitrogen content of the fuel. NO_x and N_2O final concentrations and rate of conversion of fuel nitrogen to oxides depend upon a number of homogeneous and heterogeneous formation and destruction reactions [Armesto *et al.* 2000, Armesto *et al.* 2003]. The following formation and destruction mechanisms for NO_x are proposed by Lin and Johansen, (1997):

Formation:

Nitrogen in the form of amino groups is emitted as ammonia during combustion and is converted to NO by the following reaction.

$$NH_3 + O_2 \rightarrow NO \quad (2.2)$$

$$N_{char} + O_2 \rightarrow NO \quad (2.3)$$

Reduction:

$$NO + char \rightarrow N_2 \quad (2.4)$$

$$NO + CO \text{ ------- } char \rightarrow N_2 \quad (2.5)$$

$$NO + NH_3 + O_2 \rightarrow N_2 \quad (2.6)$$

NH_3 reacts selectively with NO in the gas phase to produce N_2 and water by the following reaction [Olofsson, *et al.* 2002; Fryda, *et al.*, 2006]:

$$4NH_3 + 6NO \rightarrow 4N_2 + 6H_2O \quad (2.7)$$

Since largely only fuel NO_x is formed depending upon the fuel nitrogen content, overall NO_x emissions in fluidised beds are lower than those from fixed beds and other combustion systems [Peter *et al*, 1999]. Conversion of fuel nitrogen into NO_x depends upon chemical processes and for low NO_x formation, a reducing atmosphere is required in the furnace during volatiles burning. That is why in low NO_x burners combustion air is fed into the furnace in stages at different levels [Elmar, 2007].

Amount and quality of char, and the ash derived CaO, MgO and Fe_2O_3 in the bed act as catalysts, especially under fuel rich conditions, for NO_x and N_2O reduction. During de-

volatilisation organically bound fuel nitrogen is divided between char-N and volatile-N in the form of HCN or NH_3. The distribution of N between volatiles and char is roughly proportional to the volatile matter in the fuel [Lin and Johansen, 1997, Hupa, 2004]. Nitrogen in biomass is mainly released as NH_3 because biomass contains major portion of N as amino groups while N in high rank coals is mainly released as HCN [Saatamoinen *et al*, 1997, Mann *et al.* 1992]. Amino groups are decomposed at lower temperature to produce NH_3, while char N releases NO, N_2 and N_2O [Fryda *et al.* 2006]. Higher the volatile matter content of the fuel, lesser the char input from the fuel and the result is lower reduction in NO_x emissions due to catalytic effect of char; see Figure 2.8, which plots NO_x emissions as a function MBM% in the fuel blends for the co-combustion of Greek Lignite and Colombian coal with MBM. The figure shows that NO_x emissions increase with increase in MBM proportion in the blends as a result of increase in volatile matter induced by MBM.

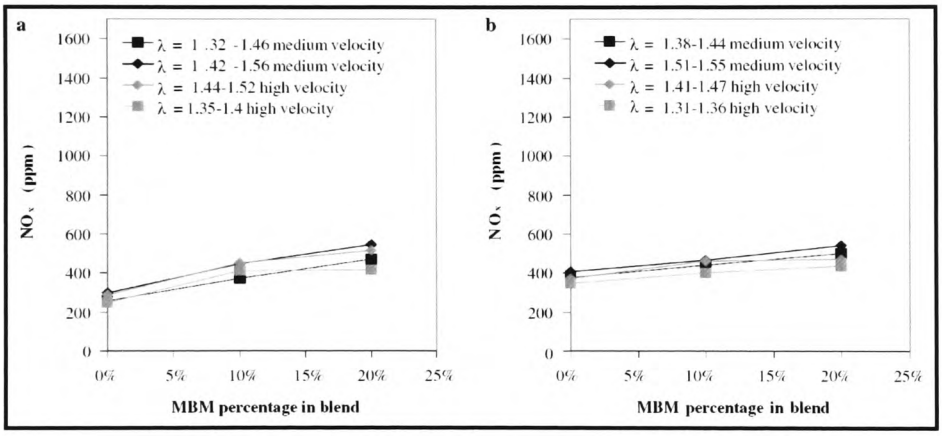


Figure 2.8: NO_x emissions from co-combustion with MBM (corrected to 6% O_2) (a) lignite (b) Colombian coal [Fryda *et al.* 2006]

Limestone addition to the fluidised bed combustor has been shown to reduce N_2O emissions and to increase the NO_x emissions. It is believed that Na_2O acts as a catalyst in a same way as CaO. Coal ash also has catalytic effects [Olofsson, *et al.* 2002]. During fluidised bed combustion the existence of ash derived CaO, MgO and Fe_2O_3 in the fuel can lead to the formation of an active bed which can catalyse the reduction of N_2O and NO_x particularly in the fuel rich conditions [Fryda *et al.* 2006]. NO_x formation due to oxidation of nitrogen containing components is favoured by CaO which acts as a catalyst under oxidising conditions. NO can also be transformed into molecular nitrogen by reaction with CO,

catalyzed by CaO, char and ash [Kopsel, 1997]. Most of these reactions are catalytic. The relative importance of these reactions, consequently determine the resultant nitrogen oxide emissions [Furusawa, 1985].

Char reduces NO_x emissions by catalytically converting NO_x to N_2. In FBC NH_3 may be formed on the bed surface due to improper fuel mixing in the bed which could homogeneously destroy the NO_x produced from within the bed by reaction 2.6 or further give NO_x by reaction 2.2. Nitrogen to NO_x conversion reduces with increased char input [Fryda *et al.* 2006]. Olofsson, *et al.* (2002) found that it was difficult to minimize both NO_x and N_2O at the same time. NO_x emissions would increase and N_2O emissions would decrease when the temperature is increased. However, no effect of pressure on NO_x and N_2O emissions was observed. N_2O emissions decrease sharply with increase in temperature [Armesto *et al.* 2003] due to a decrease of volatile NCO (derived from HCN) which will react with NO to form N_2O. Higher the temperature, higher the NO and lower the N_2O [Fryda *et al.* 2006]. Below 900 °C, N_2O emissions are expected to be above 20 ppm [Makarytchev *et al.* 1995].

Leckner and Lyngfelt, (2001) have found that reduction of bed temperature leads to lower emissions of NO but emissions of N_2O increase. If the bed temperature becomes too low the concentration of unburned gases as well as that of char in the ash increases considerably. Moreover, increasing velocity enhances N_2O emissions because it shortens the contact time between char or ash particles and flue gas [Fryda, *et al.*, 2006].

Co-firing of coal with biomass can reduce NO_x emissions. If secondary fuel has lower nitrogen content, NO_x emissions will be lower and vice versa. If the proportion of the secondary fuel is increased, nitrogen conversion to NO_x is decreased. Hein and Bemtgen [1998] noted that co-firing of wood and coal reduced NO_x emissions because of the lower fuel N content of wood. They observed that NO_x emissions decreased considerably with increased wood input.

Dong *et al.* (2002) observed during co-firing MSW and bituminous coal that emissions of NO and N_2O decrease sharply with the introduction of MSW, see Figure 2.9. According to them this could be due to the combustion of MSW induced volatiles which reduces the diffusion of oxygen to the char surface and results in the promotion of nitric and nitrous reduction

reactions. Reduction of N_2O to N_2 can also due to radicals (H and OH) coming from the combustion of volatiles. The presence of sodium, calcium and potassium in MSW can also catalytically decompose N_2O. With increase in MSW mixing ratio (R) N_2O increases slightly possibly due to lower temperature zone around the particles. They obtained higher NO and lower N_2O emissions with increase in bed temperature, see Figure 2.9C. Higher freeboard temperature due to MSW volatiles combustion promotes the reduction of N_2O and oxidation of NO. At higher bed temperature concentration of char decreases and NO reduction reactions on the char surface are suppressed.

When co-firing coal with MSW, NO emissions slightly increase with increasing waste fraction from 0 to 30% [Suksankraisorn, *et al.*, 2003] despite the lower overall fuel nitrogen content. This could be due to higher ammonia (NH_3) release and conversion to NO, the presence of less char particles (char reduces NO_x emissions by catalytically converting NO_x to N_2) in the bed to reduce NO or an increase in O and OH radicals (to react with NH to form NO) due to higher moisture in MSW.

McIlveen-Wright and co-workers [McIlveen-Wright*et al.* 2007] have demonstrated by working on six combustion systems of different sizes and firing techniques (including pulverised fuel combustion system, circulating fluidised bed combustion systems from 12 to 250 MWe, pressurised fluidised bed combustion system) with different fractions (from 0 to 100%) of biomass of different types (including straw, wood, sewage sludge, woody matter from olive stones) that the statutory Emission Limit Value (ELV) for NO_x after 2016 (set to be 200 mg/Nm^3) can be achieved by co-firing biomass with coal. A contributory factor is that biomass, usually, contain more moisture than coal which reduces bed temperature and consequently NO_x emissions [McIlveen-Wright *et al.* 2007].

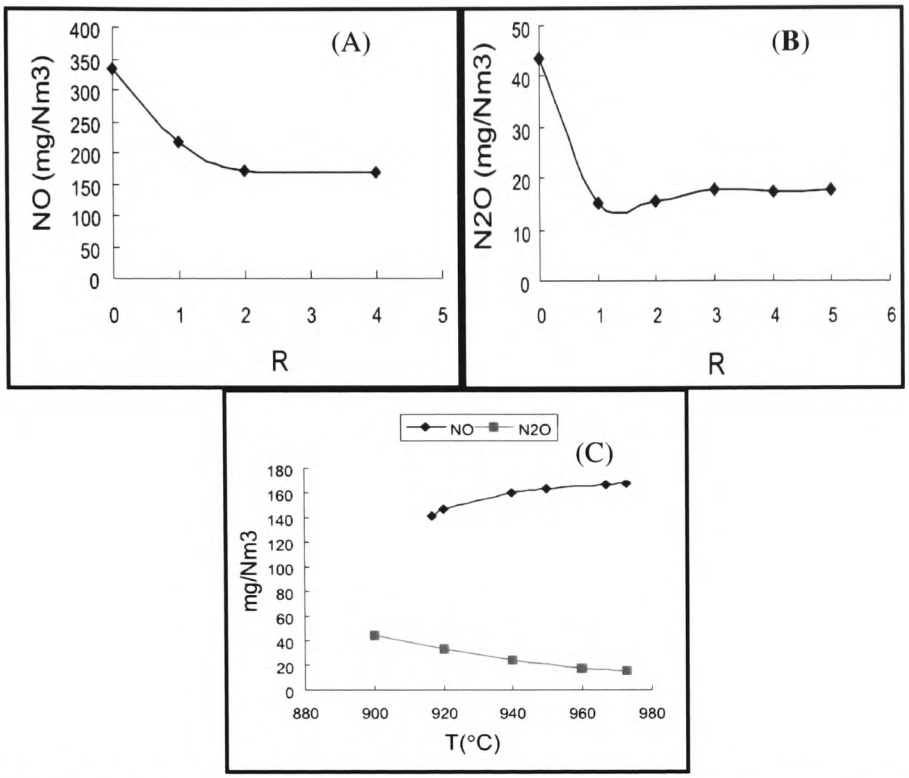


Figure 2.9: Emissions of NO and N_2O as function of mixing ratio (R) (Figures A and B) and bed temperature (Figure C) [Dong *et al.* 2002]

Olofsson, *et al.* (2002_b) studied the influence of three fuel additives ammonium bicarbonate (NH_4HCO_3), urea ($CO(NH_2)_2$) and sodium carbonate (Na_2CO_3), 5% (wt/wt), for repressing the formation of NO_x and N_2O during combustion of straw, MBM, sawdust and willow in a pressurised fluidised bed combustor of 90 kW_{th} with a gas velocity of 0.25 – 0.3 m/s and residence time of 11 to 13.2 seconds using fyle sand, magnesite, bone ash and mullite as bed materials. They found most important factor for the NO and N_2O emissions was fuel type, followed by the bed material and NO_x repressing additive. The conversion of fuel nitrogen to NO_x (9 – 16%) and N_2O (15 – 21%) was different for different fuels see, Table 2.10. Higher conversion to N_2O was found to be due to lower combustion temperature <900 °C. Bone ash was the best material for both NO and N_2O minimisation due to the catalytic effect of a high content of CaO (44.8%). CaO is also an active catalyst for the formation of NO but if the right conditions (presence of CO and char) for the degradation reactions exist the net result can be a decrease in NO and N_2O emissions. Desroches-Ducarne, *et el.*, (1998) found that NO emissions from MSW combustion was higher than that from coal although the nitrogen

content of the coal was higher (1.3%) than the MSW (0.6%). N_2O increases gradually with coal fraction. When coal is added to MSW, the rate of formation of NO_x decreases since the combustion rate decreases and char concentration increases which results in increased rate of NO_x reduction reaction. When the coal fraction exceeds 30%, the CO concentration also increases. Carbon (C) and carbon monoxide (CO) reduce NO and less NO is available to be converted to N_2O. Also N_2O decomposition on the char surface takes place.

Nitrogen content, a significant factor affecting the NO_x emissions, is relatively high in waste fuels such as leather waste (14.4% DAF basis) and MBM (7.8% DAF basis) [Svoboda *et al.* 2006] and the heating value is low which may result in higher NO_x emissions. Emissions of NO_x in BFB boiler can be reduced to relatively low levels by maintaining low combustion temperatures between 700 – 900 °C. For example, Wiktorian & Tarnawski, (2004) demonstrated that bark combustion in BFB boilers produces only small amounts of SO_2, NO_2, and CO. The emission factors for bark and wood waste combustion in the BFB boiler are given in Table 2.11. The long residence time of the fuel particles in the combustion zone yields low CO emissions and normally CO is below 100 and 200 mg/Nm^3. An important factor in keeping the CO levels low with low excess air is even fuel feed rate. The boiler can be operated at 20 – 25% excess air level thus maintaining the emission levels of CO (33 – 82 mg/m^3) and NO_x (270 – 370 mg/m^3). NO_x emissions in wood-sludge combustion typically vary between 200 – 300 mg/Nm^3 depending upon fuel nitrogen content and operating conditions so again can be maintained within acceptable limits.

Table 2.10: Conversion of Fuel-N to NO and N_2O [Olofsson, *et al.* 2002b]

Fuel	N-Conversion to NO		N-Conversion to N_2O	
	1.0 Mpa	1.5 Mpa	1.0 Mpa	1.5 Mpa
Sawdust	15	3	21	2
Straw	13	19	n.a	8
Willow	16	8	15	10
MBM	9	n.a	18	n.a

Table 2.11: Emission factors for the BFB boiler burning bark [Wiktorian Tarnawski, 2004]

Factor sources	BAT	BFB boiler in Poland	BFB boiler in pulp and paper mill in Poland
SO_2	5 – 15 mg/MJ of fuel	75 – 12 g/GJ of fuel	Limit <90 mg/m^3 Result 30 – 70 mg/m^3
NO_x	40 – 100 mg/MJ	90 – 119 g/GJ	Limit <370 mg/m^3 Result 270 – 370 mg/m^3
CO	-	10 – 350 g/GJ	Limit <200 mg/m^3 Result 33 – 82 mg/m^3

The formation of HCl is promoted when Cl, S, H_2O and O_2 coexist. HCl emissions therefore increase with the increase in MSW proportion. When MSW is fed into the CFB, NO and N_2O decrease abruptly. Although at a specified MSW fraction NO increases while N_2O decreases with increasing bed temperature and the High NO emissions are due to the effect of higher temperature in the dilute region. The Higher temperature promotes the reduction of N_2O and the oxidation of NO. For a constant fuel mixing ratio NO emissions increase, SO_2 and HCl remain constant but N_2O emissions decrease with increasing temperature [Dong *et al.* 2002].

To sum up under fluidised bed operating conditions (850 to 950 °C) thermal NO_x is not formed and fuel NO_x dominates. Thus overall NO_x emissions in fluidised beds are lower than those from fixed beds and other combustion systems. Co-firing of coal with biomass can reduce NO_x emissions if secondary fuel has lower nitrogen content or increase NO_x emissions as a result of increase in biomass induced volatile matter. Higher the volatile matter content of the fuel, lesser the char input and the result is lower reduction in NO_x emissions due to catalytic effect of char which reduces NO_x emissions by converting NO_x to N_2. Also, higher freeboard temperature due to combustion of biomass volatiles promotes the reduction of N_2O and oxidation of NO. Amount and quality of char in the bed acts as a catalyst, for NO_x and N_2O reduction, especially under fuel rich conditions. It is difficult to minimize both NO_x and N_2O at the same time as NO_x emissions increase and N_2O emissions decrease when the temperature is increased. Limestone addition to the fluidised bed combustor can reduce N_2O

emissions and increase the NO_x emissions. Increasing velocity enhances N_2O emissions because it shortens the contact time between char or ash particles and flue gas.

2.9 Commercial facilities operational on high moisture biomass:

The earlier sections of this review have demonstrated that biomass materials, even with high moisture contents, can be burnt or co-fired with a supplementary fuel such as coal or peat. Consequently the next sections will summarise some of the commercial scale facilities which have been installed.

A CFB boiler has been built in Swiecie (Poland) to burn a blend of wood waste (bark and saw dust) having moisture contents variation from 45 to 65% and coal with a corresponding range of lower heating values between 6.7 and 27 MJ/kg. The boiler is designed to burn proportion of waste wood to coal from 0 to 100%. The plant has been operated on biomass only with up to 200 tph loads having LHV as low as 5.4 MJ/kg [Elmar, 2007].

A CFB boiler in Neumünster (Germany) rated at 75 MW_{th} was designed to burn varying proportions of coal and RDF (moisture 7 – 38%, ash 10 – 24%, LHV 10 – 20 MJ/kg, bulk density 100 – 350 kg/m^3) coming from a mechanical biological treatment plant. It can also be operated on 100% coal so that the plant can be operated on LHV between 10 and 30 MJ/kg. The plant can also be operated on natural gas, fuel oil or bituminous coal in case no waste is available. The plant is based on the experience of the previous RV Lenzing plant that was the first plant using CFB technology to burn 100 % RDF and other waste fuels [Elmar, 2007].

The largest BFB boiler operating in North America at Pacifica Paper, was designed by Foster Wheeler and rated at 73.7 kg/s steam at 6205 kPa and 477 °C. It is capable of burning fuel blends of hog fuel (bark), primary and secondary mill effluent sludges having high moisture, low energy and also sea salt contamination. The analysis of the fuels used and operating conditions are given in Table 2.12. They observed excessive temperature swings when fired the boiler with 60% moisture fuel and partially dried it to 20 – 30% moisture to solve the problem [Wu, *et al.* 1999].

2.9.1 Commercial facilities running on Meat Industry wastes:

There appear to be relatively few commercial facilities in the world burning or co-firing poultry derived wastes. In the UK, according to the report published by Northern Ireland Assembly [Jeff, 2008], there are four electrical generation plants operated by Energy Power Resources (EPR). Details of the facilities are given in Table 2.13.

Table 2.12: Typical Fuel properties and conditions of Pacifica Paper BFB boiler [Wu, *et al.* 1999]

	Hog[1]	Hog[2]	Sludge	Hog + Sludge (10:1, mass ratio)
Proximate analysis				
Fixed carbon (%)	18.58	19.85	14.97	18.15
Volatile matter (%)	56.79	59.72	45.35	54.61
Ash (%)	2.43	1.87	16.76	4.97
Moisture (%)	22.2	18.56	22.92	22.26
Ultimate analysis				
Carbon (%)	40.62	42.99	33.28	40.94
Hydrogen (%)	4.51	4.8	3.78	4.5
Oxygen (%)	30.08	31.62	21.58	26.98
Nitrogen (%)	0.13	0.13	1.49	0.31
Sulphur (%)	0.03	0.03	0.19	0.03
Cl (%)	0.24	0.31	0.11	0.22
HHV (MJ/kg)	15.96	17.22	13.19	15.32
Operating conditions				
Test duration (hrs)	12.5	26.5	100	-
Nominal bed temperature (°C)	850	790	780	-
Primary air velocity (m/s)	1.3	1.3	1.3	-

E.On power plant in Netherlands (Maasvlakte) utilises 150,000 tonnes MBM per year. Essent power plant in Borselle co-utilises MBM with coal. Co-combustion of 25% MBM has been carried out on a 200 MW_{th} district heating plant having two FBC units in Andrestrasse by a German company Energieversorgung Offenbach AG [Fryda *et al.* 2006].

More recently in 2008, a fluidised bed boiler and steam cycle plant of 36 MW capacity burning poultry litter at a rate of 400k tpa has started operation in Moerdijk, Netherlands. Also Fibrowatt power station in Minnesota is the first poultry litter power station in USA having 55 MW capacity consuming 500k tpa poultry litter. Both of these plants produce high quality fertilizer as a by-product [Jeff, 2008]. Several additional power plants have been proposed in the USA, The Netherlands, Ireland and Western Australia, with further sites being investigated in Belgium, France, Germany, Italy, Portugal and Spain. In the Netherlands a fluidised bed gasifier for poultry litter rated at 60 kWe was commissioned in 2001 and produces heat for use on a farm and electricity for a grid [Florin, *et al.* 2009].

2.9.2 Commercial facilities running on Sludge:

Two olive husk fired, 16 MWe power plants, are located in Villarta de San Juan and La Loma (Spain). Both have grate combustion systems. Other facilities in Spain are a 25 MWe capacity in Baena, and a 5 MWe in Algodonales both with rotary grate systems for olive husk combustion. There are two more plants in Palenciana, one of 12.5 MWe using wet olive husk (60% wet basis) in a fluidised bed boiler and another one of 5.7 MWe using dried olive husk in a conventional boiler. Another plant in Lucena, works in association with an oil mill and a grape-seed oil extraction plant producing about 15000 t/y dry olive husk as residue. The plant is based on a 14.3 MWe gas turbine generator package, an olive oil residue incinerator and heat recovery system, and a 14.8 MWe steam turbine generator package. A sludge drying plant using a grate fired water tube steam boiler in Villanueva de Algaidas has a capacity of 150000 t/y, and works on combined cycle and generation of 9.15 MWe electric power from olive husk and eventually from waste matter after olive grove pruning [Celma *et al.* 2008].

Table 2.13: Electricity generation plants in UK using poultry litter as fuel [Jeff, 2008]

Company	Location	Capacity MW	Poultry litter usage tpa	Technology	Importance
EPR¥	Suffolk* UK	12.7	140,000	Moving grate boiler and steam cycle	World first poultry litter fuelled generating plant
EPR	Glanford UK	13.5	89,000	Moving grate boiler and steam cycle	Worlds second poultry litter fuelled generating plant
EPR	Fife, Westfield UK	9.8	110,000	Bubbling Fluidised Bed	First biomass fuelled generator in Scotland
EPR	Norfolk UK	38.5	420,000	Moving grate boiler and steam cycle	World's largest poultry litter fuelled plant in the world and largest biomass fuelled electricity generator in Europe

EPR¥ – The Energy Power Resources Limited

*Also produces high quality fertilizer as a by-product

2.10 Sugar Industry Co-Products:

This review has considered combustion or co-firing of a number of different biomass materials particularly those with high moisture contents. However the main study of the experimental work in the thesis is the co-firing of pressed sugar beet pulp a co-product of the sugar industry so that the rest of the review concentrates on sugar industry products.

A third of world's sugar production comes from sugar beet with the remainder coming from sugar cane. European norms define the sugar beet as marketable if it contains 14% sugar or more. The standard sugar beet should have a sugar content of 16% [FAO, 2009]. The rest of the material, after extracting alcohol and some other chemicals, goes to different by-products

of the process which are of a relatively low economic value. They include vinasse, raffinate and sugar beet pulp.

The root of the beet (taproot) contains 75% water and 25% dry matter. The dry matter comprises about 5% pulp. Pulp, insoluble in water and mainly composed of cellulose, hemicellulose, lignin and pectin, is used in animal feed. Sugar represents 75% of the root's dry matter [FAO, 2009]. Typically one tonne of sugar beet provides a dried weight of 130 kg of sugar and 50 kg of sugar beet pulp [Rouilly *et al.* 2006a] rest is water (around 75% weight of the cleaned sugar beet) and molasses.

Sugar production from cane gives bagasse as a byproduct instead of pressed pulp. Bagasse is the crushed remnants of sugar cane stalks left after the extraction of juice [Rasul and Rudolph, 2000]. Bagasse is of higher economic value as compared to byproducts of beet processing. In the following paragraphs different by-products of the sugar industry are discussed with respect to their importance and application as a potential source of energy.

2.10.1 Bagasse:

The most widely used sugar industry co-product is bagasse from sugar cane processing. Typical composition of bagasse is given in Table 2.14. Every 1 tonne of raw sugar production gives 2.7 tonnes of bagasse [Zandersons, *et al.* 1999]. Bagasse is a high thermal fuel only if it is dried since the lower heating value of raw bagasse is 5.4 MJ/kg [Drummond and Drummond, 1996]. However the specific energy of dry ash free bagasse is around 19.3 MJ/kg [Rasul and Rudolph, 2000]. At 12% moisture and 7% ash its energy value is 18.4 MJ/kg [Calvin, 1966]. The Bulk density of bagasse is 70 – 200 kg/m^3 [Zandersons, *et al.* 1999] and its particle density is 492 kg/m^3 [Rasul and Rudolph, 2000].

Bagasse from sugar cane represents a high value by-product, which can be burnt for the production of power or can be used for obtaining paper or other composite materials. The possibility of using sugar cane bagasse for the production of paper is well known [Vaccari, *et al.* 2005]. Large and medium sized sugar mills typically use about 75% of their bagasse as fuel to satisfy their energy needs with the surplus used for paper, pulp and board manufacture [Mobarak *et al.* 1982].

Table 2.14: Typical Composition of Bagasse

	Begasse[1]	Begasse[2]	Begasse[3]
Proximate Analysis			
Fixed carbon (%)	6.1	18.35	12.11
Volatile matter (%)	40.2	n.a.	65.24
Ash (%)	1.7	1.5	2.65
Moisture (%)	52	50	20
Ultimate Analysis			
Carbon (%)	23.8	23.5	49.66
Hydrogen (%)	2.8	3.25	5.71
Oxygen (%)	20.1	21.75	41.08
Sulphur (%)	Trace	0	0.03
Nitrogen (%)	Trace	0	0.21
Heating value (MJ/kg)			19.04

[1]Cortez and Perez (1997)

[2]Narayanan and Natarajan (2006)

[3]Santos, (2004)

Bagasse is an important potential source of energy [Rasul and Rudolph, 2000]. Fuel moisture plays a very important role in the design and performance and the initiation of instability in bagasse fired furnaces, [Norman, 1987]. It is observed that sudden changes in the bagasse moisture due to operational problems appear to have a great effect on the furnace behaviour [Shanmukharadhya. and Sudhakar 2007]. Because of the high moisture content (45 – 55%) combustion of as received bagasse can be ineffective and unstable process [Kuprianov *et al.* 2005] thus causing maintenance problems [Woodfield *et al.* 2000]. Kuprianov *et al.*, for example, failed to burn bagasse in preliminary tests due to high moisture (48.8%). But stable operation was achieved for a wide range of operating conditions when the bagasse was dried to a moisture content of 14.4% on ash free basis.

Bagasse can also be transformed into useful products such as oil and char by pyrolysis [Piskorz *et al.* 1998] and has also been gasified to generate synthesis gas for catalytic

conversion to diesel oil [Sood, 1994]. Char obtained from bagasse pyrolysis can be used as feedstock for the production of activated carbon [Bernardo *et al.* 1997].

Zandersons, *et al.* (1999) studied the production of high quality charcoal from bagasse in a thermo-reactor. The bagasse specimens for thermolysis were briquetted (18 – 20 g of bagasse briquettes measuring 120 * 15 * 15 mm) at ambient temperature without the use of a binder (moisture content 6.2%, pressure 1000 kgf/cm^2) and heated electrically from 100 to 600 °C. The results of char yield and fixed carbon content were measured as a function of peak bulk temperature and reactor wall temperature. They found that the critical point of the process is the heating rate in the temperature range from 200 to 350 °C. At a reactor wall temperature of 500 °C the charcoal yield and fixed carbon content are 23 and 17.4% respectively (dry bagasse basis). If the wall temperature is 550 and 600 °C there is not only a considerable drop in the charcoal yield (from 23.0% at 500 °C to 20.2 and 20.7%, respectively) but its fixed carbon content is also lower (13 and 15.9%, respectively). They however, concluded that due to extremely low bulk density of the bagasse charcoal (76 – 108 kg/m^3) it is a difficult material for further processing. Catalytic activity of ash components, on the charcoal yield, has been reported by [Scott *et al.* 1985] but was not observed by Zandersons *et al.* (1999).

Hans Darmstadt *et al.* (2001) also studied pyrolysis and concluded that co-pyrolysis of bagasse under vacuum with 15% or less of petroleum residue yields a char which is a suitable feedstock for the production of high surface area activated carbon. They found that the bagasse char contained 18.9% volatiles and has a specific surface area of about 530 m^2/g. In addition to these studies on the production of secondary products other investigators have looked at the combustion or co-firing of bagasse and these are now reviewed.

For example, in an early study Magasiner, (1987) analysed the performance of a sugar mill (Lonrho Sugar Corporation Limited's Britannia Mill in Mauritius) boiler fired with bagasse having a moisture content of up to 56 %. They found that an air preheater was progressively brought into operation in the moisture range of 34 – 47% and was fully utilized in the range 47 – 56%. For a given thermal rating the unburned carbon loss increases rapidly as the moisture content increases. See, for example, Figure 2.10 which shows drop in efficiency as a function of fuel moisture for a baggase fired boiler. Magasiner proposed the use of a

refractory lining in the ignition zone to minimise heat losses and hence promote combustion stability when burning high moisture fuels.

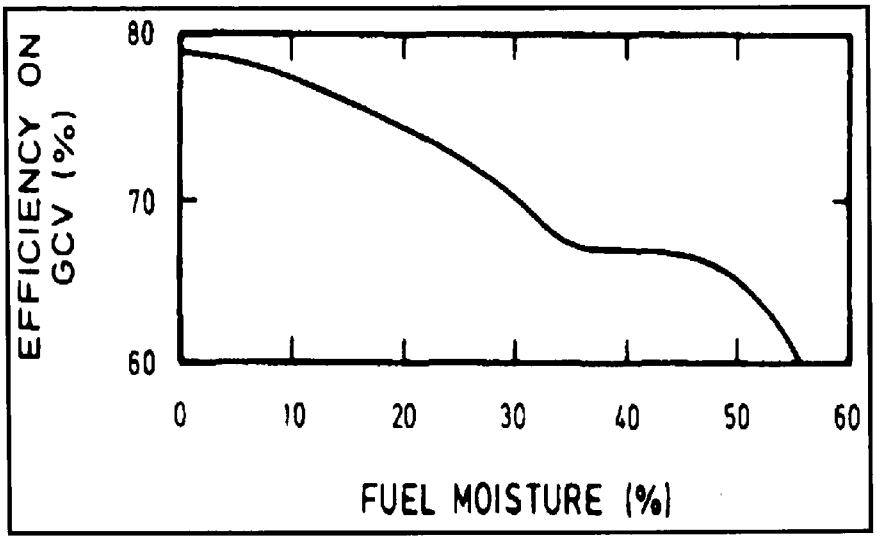


Figure 2.10: Efficiency Vs. Fuel moisture for a bagasse fired boiler, Magasiner, (1987)

Woodfield *et al.* (1999a) investigated the effect of fuel moisture on the combustion stability in the furnace of 109 MW boiler, having dimensions of 18.3 m high, 9.46 m wide and 7.56 m deep. Bagasse distributors were evenly spaced 2 m above the grate to feed in the fuel with a characteristic particle size of 2.4mm. Secondary air was provided at front and rear of the boiler to assist combustion. Nevertheless they observed unstable combustion at high bagasse loadings because of inadequate drying of the bagasse particles. These authors have demonstrated that CFD modelling can predict the critical moisture content, for a given set of conditions, at which ignition becomes unstable. The critical moisture content used as an ignition criterion was set to 15% in the CFD simulation. Generally, a primary source of instability is high moisture content of the fuel which causes an ignition delay. This results in unburnt bagasse accumulating on the grate, and drying and burning in a periodic manner. The problem exacerbates if non-uniform supply occurs from the bagasse feeders and the air distributor pressure is not adequate. Under such conditions combustion can be intermittent over the majority of the grate area so that large unburnt bagasse deposits can build up and for example, [Dixon, 1983] reported that deposits higher than 1 m are common.

Shanmukharadhya and Sudhakar (2007) found a low temperature region on the travelling grate of a spreader stoker furnace as a result of ignition delay caused by drying and heating up of bagasse. However they did not observe any signs of gross flame instability when the moisture content of the bagasse was below 54%. However combustion was unstable at higher moisture contents. This confirms the observations of Luo and Stanmore, (1994) who found that burnout took place at a bagasse moisture content of 60%.

Luo, (1993) measured the thermal efficiency of a sugar mill boiler to be 62% because of the high moisture content of bagasse. The low efficiency combustion technology (mostly grate fired) employed by Kuprianov *et al.* (2005) also resulted in similar results. If fluidised bed combustion could be used for bagasse combustion, a 20 – 25% improvement in efficiency could be expected [Das and Bhattacharya, 1990] since fluidised bed combustion is expected to be the most efficient among the combustion technologies used for firing biomass fuels [Werther *et al.* 2000; Bhattacharya, 1998]. A properly designed fluidised bed combustor should provide better combustion performance as compared to traditional methods such as grate or swirl burner technologies.

However attempts to burn as received sugar cane bagasse in a fluidised bed system are reported to be unsuccessful due to its high moisture content and operational problems have been reported particularly related to feeding, see Permchart and Kouprianov, (2004). However, after pre-drying sugar cane bagasse can be fired with about 99% combustion efficiency and lower environmental impact [Permchart and Kouprianov, 2004; Kuprianov *et al.* 2005]. Rasul and Rudolph, (2000) tried to develop an energy efficient method of power generation from sugar cane bagasse using FBC. This study concentrated on the issue of segregation problem which is observed practically during combustion in fluidised beds containing blends of bagasse and inert particles. For proper mixing of bagasse with bed material the inert fluidising solids must be denser than bagasse and with a terminal free-fall velocity smaller than that of bagasse. Possible inert materials which may satisfy this criterion include pumice, porous alumina, cenolyte and expanded clays. Thus, if the properties of one the particles are given, then the other particle can be selected to avoid segregation. More specifically, knowing the aerodynamic properties of bagasse, suitable inert fluidising solids can be selected to achieve successful fluidisation and proper mixing of bagasse, essential for efficient combustion in a fluidised bed. Based on the model and theoretical bulk density

evaluation they proposed that a blend of cenolyte (64 mm, 690 kg/m^3) and bagasse (200 mm, 492 kg/m^3) satisfy the above criteria within U_{mb} of cenolyte.

In a later paper Kuprianov *et al.* (2006) co-fired as received sugar cane bagasse (moisture 48.8%) and rice husk (moisture 11%) in a fluidised bed combustor. The feed rate was about 82.5 kg/h and various excess air levels (40, 60, 80 and 100%) were used for different rice husk energy factions (0.6, 0.85, 1.0). They failed to burn as recieved bagasse on its own and with small fractions of rice husk due to bed cooling below the temperature of stable ignition. At a rice husk energy fraction of 0.6 the bed temperature was relatively low, 650 – 670 °C, but fuel ignition and combustion was quite stable. With pure rice husk, the unburned carbon content was found to vary from 8.1 to 10.6% with excess air variation of 39.7 to 100.2%, respectively, due to reduced residence time of fuel particles during their transportation in the relatively short combustor they used. The loss with unburned carbon is reduced with higher mass fractions of bagasse in the blend. With a rice husk energy fraction of 0.85 (mass level of 75%) they found a maximum combustion efficiency of 96.12% at an excess air of 80%. Kuprianov *et al.*, found that co-firing of sugar cane bagasse with over 45% rice husk (wt/wt) resulted in sustainable combustion with 95 – 96% combustion efficiency and with lower NO emissions than pure rice husk. Excess air levels of 50 – 60% were found to be optimum for high combustion efficiency and minimum environmental impact at the maximum combustor load.

A thermo-graphic analysis of sugar cane bagasse pyrolysis showed that emissions of volatiles start at 205 °C and the maximum rate of decomposition of hemicelluloses and cellulose in the fuel takes place at 305 and 350 °C, respectively [Silva and Soler, 1988]. A particle of size 0.5 to 1 mm can be heated up to 400 °C in 0.16 to 0.36 sec, but a coarser particle of size 2 – 3 mm takes 1.3 – 2.8 sec [Shubeko and Yenik, 1974]. Depolymerisation reactions of fine particle cellulose occur in the temperature range of 200 – 300 °C [Zandersons, *et al.* 1999]. They observed that during drying of raw bagasse (moisture 50 – 65%) a considerable amount of volatile products is formed. They obtained 50 – 80 % of volatiles during the drying stage when temperature inside the bulk of bagasse was not higher than 200 °C. During heating up and pyrolysis stage at 270 – 280 °C, exothermic reactions start and at a temperature of 350 – 400 °C the natural molecular structure of lignocelluloses biomass is degraded [Levin, 1980].

The summary of the above discussion is that Bagasse represents a high value by-product, which can be used for power production, paper production, can be transformed into useful products such as oil and char by pyrolysis and can also be gasified to generate synthesis gas for catalytic conversion to diesel oil. Char produced by pyrolysis and co-pyrolysis of bagasse with petroleum residue under vacuum is a suitable feedstock for the production of high surface area activated carbon. Combustion of as received bagasse can be an ineffective and unstable process because of its high moisture content which causes an ignition delay. Conventional combustion systems give lower combustion efficiency due to high moisture content of bagasse, however, fluidised bed combustion technology can be used to improve combustion efficiency. A properly designed fluidised bed combustor should provide better combustion performance as compared to traditional methods such as grate or swirl burner technologies. However, attempts to burn as received sugar cane bagasse in a fluidised bed system are reported to be unsuccessful due to its high moisture content and operational problems have been reported particularly related to feeding. Pre-dried bagasse has been successfully fired in fluidised bed with about 99% combustion efficiency and lower environmental impact. Co-combustion of bagasse with rice husk in a fluidised bed has also been proved to be successful.

2.10.2 Vinasse:

Vinasse also known as distillery wastewater, stillage, slops and dunder is another by-product of the sugar industry. Molasses from the sugar manufacturing process is used to produce alcohol and the remaining liquor after alcohol extraction is termed as vinasse [SAACKE, 2009]. Vinasse may have widely different properties depending upon the process and raw material used for the production of alcohol as shown in Table 2.15. For example, vinasse characteristics vary significantly if molasses comes from cane sugar rather than the beet sugar industry. The raw diffusion juice which is rich is organic and inorganic substances has an acidic PH and is deeply turbid and coloured. Distilleries produce huge amounts of vinasse with a medium sized distillery processing 110,000 – 120,000 tonnes of molasses per year producing about 70,000 tonnes of concentrated (60 Brix) vinasse per year [Vaccari, *et al.*, 2005].

One of the reasons limiting the spread of the biotechnology industry is the production of wastes, e.g. vinasse, which are difficult to dispose off. The large amount of vinasse can be utilised as fodder which partially solves the problem.

Table 2.15: Characteristics of Brazilian distillery wastewater
[Sheehan and Greenfield, 1980]

	Distillery feedstock		
Characteristics	Cane molasses	Cane juice	Cassava
Organic matter	63.4	19.5	21.8
Total nitrogen	1.2	0.3	0.4
Sulphate $(SO_4)^{-2}$	8.4	0.6	0.1
Calcium (CaO)	3.6	0.7	0.1
Phosphorus (P_2O_5)	0.2	0.2	0.2
Magnesium (MgO)	1	0.2	0.1
Potassium (K_2O)	7.8	1.2	1.1

Vinasse constitutes a high volume high strength acidic waste so that disposal of untreated vinasse to natural waterways is not feasible [Sheehan and Greenfield, 1980]. Vinasse is probably the strongest of all industrial wastes in terms of its polluting load specially B.O.D. Average B.O.D of vinasse from a molasses distillery is about 35000ppm. A small distillery discharging only 50,000 gallons of vinasse per day can contribute a B.O.D load equivalent to the sewage of a town with 100,000 inhabitants. To maintain about 3ppm dissolved oxygen in the stream receiving the waste minimum dilution required is 11660 times that of the waste or about 11000 cusec (cubic feet per second) of water [Chakrabarty, 1964]. Verma and Dalala [1976] have noted that the waste poses significant threat to fish. They have found LC50 values of vinasse that can kill different fish species in 96 hours.

Vinasse, typically, contains a high concentration of potassium, calcium, chloride and sulphate ions. Inorganic constituents present in vinasse are given in Table 2.16. Ash from the combustion of vinasse contains about 37% K_2O and 70 – 73 % of the ash is soluble in water.

Potash is present as sulphates, chlorides, sulphides and carbonates. The average distribution of potassium salts in the ash is given in the Table 2.17 [Sheehan and Greenfield, 1980].

Different options have been tried or proposed to utilize vinasse. Possible outlets for this by-product could be composting, fodder, filler in paper, cattle feed, methane production by anaerobic fermentation, fertilizer (high K content), as a binder in briquetting and combustion.

Table 2.16: Inorganic constituents in molasses stillage (g/kg)[Bieske, 1979]

	Australia	Brazil
Component	Millaquin distillery	Average (1976)
Ash	32	19.2
N	3.1	0.9
P	0.02	0.05
K	8.6	4
Ca	1.1	1.8
Mg	1.5	0.5

Table 2.17: Average distribution of different potassium salts in the crystals obtained from neutralisation of Vinasse ash [Sheehan and Greenfield, 1980]

	Range (%)
Potassium sulphate, K_2SO_4	66 – 68
Potassium chloride, KCl	16 – 17
Potassium carbonate, $K_2CO_3.2H_2O$	6 – 7
Total potash as K_2O	50 – 51
Total average potassium salts as %age of crystals	90

Volume of stillage can be reduced by recycling which also removes some of the organic and inorganic constituents [Sheehan and Greenfield, 1980]. About 50% of the stillage can be recycled [Dubey, 1974]. Stillage can be applied to land as a fertilizer to increase its pH because high Ca and Mg improves physical and chemical properties, mineral and water containing characteristics and fertility of soil [Sheehan and Greenfield, 1980]. A number of studies have been devoted to assess the feasibility of vinasse as a fertilizer e.g. Ross *et al.* (1938), Sastry *et al.* (1964), Guimaraes *et al* (1968), Dubey, (1974), Khuruslova *et al.* (1974), Cooper, (1975), Jackman, (1977), Gloria, (1977) Bieske, (1979) and Usher and Willington, (1979). For economic disposal of vinasse as a fertilizer a large land area adjacent to the distillery is required and should be in a low-medium rainfall region which is highly unlikely in the UK. Moreover there are huge costs of piping network [Sheehan and Greenfield, 1980]. Zajic (1971) proposed deep well disposal of vinasse as a cheaper alternative. However limited underground storage and specific geological formation preclude a wide scale stillage disposal by this method [Sheehan and Greenfield, 1980]. Montanani (1954) described a system in which stillage is neutralized with lime and evaporated to be used as a fertilizer. Dubey (1974) discussed stillage disposal with particular reference to UK where 1280 m^3 of stillage per hectare per year is required. The land is ploughed or sprinkled to control odour. Sastry *et al.* (1964) however concluded that the process is not economical if odour is a series issue.

Van Haandel (2005) discussed the feasibility of anaerobic digestion of sugarcane vinasse. The anaerobic digestion of vinasse has been applied at full scale at several distilleries [Souze, 1992] with conversion efficiencies of more than 80% at organic loading rates of over 20kg COD/m^3/d. For the amount of COD in vinasse, about 100 kg of methane is produced at 80% removal efficiency. If methane is used for power generation, 500kWh of power can be produced for a generation efficiency of 35 – 40% [Van Haandal, 2005]. However, according to Cortez and Perez (1997) economics associated with technical problems act as a limiting factor for methane gas production by anaerobic fermentation of vinasse.

Julsingha (1970) described a process for removing potassium from vinasse. Vinasse was concentrated to 30 – 60 °Brix and H_2SO_4 was added to it. Potassium was removed in the form of $K_2SO_4.5CaSO_4.H_2O$. Reich (1945) proposed a system in which concentrated stillage is passed through three low temperature carbonising retorts and activated at 870 °C. The

resultant carbon then undergoes counter-current aqueous extraction to produce potash liquor and char. The liquor contains KCl and K_2SO_4 for fertilizer use. Yamauchi, *et al.* (1977) burnt stillage containing 21% solids using heavy fuel oil. Ash was dried to produce non-hygroscopic granules to be used as a fertilizer. Sastry *et al.* (1964) reported 34.7% K_2O and 2.2% P_2O_5 in the stillage incineration ash. However, according to Monteiro (1975) incineration to produce fertilizer is not economical.

Polack *et al.* (1981) showed that combustion of Louisiana's vinasse is very difficult and they were not successful in the combustion of vinasse even when air was preheated and different air fuel ratios were tested. However, Cortez and Perez (1997) were successful in combusting vinasse alone in different solid concentrations and in co-firing 45° Brix as an emulsion with #6 fuel oil. Vinasse used for the tests was from Shepherd oil distillery and its composition is given in Table 2.18. They determined that the adiabatic flame temperature of 50% solids vinasse was 700 °C and that of 60% solids vinasse was 793 °C.

They combusted vinasse and #6 fuel oil emulsion in different concentrations and concluded that the combustion of the emulsion was feasible when vinasse concentration in the emulsion was varied from 0 to 50% with best results obtained for vinasse concentrations up to 25%. However, when vinasse concentration was increased above 50% they observed that the flame was unstable. They measured CO as a function of excess air and found that when concentration of vinasse in the emulsion is increased, CO concentration in the flue gas tend to stabilize. For emulsions with 20% or higher vinasse content, CO concentration tend to reach a constant value of about 105 – 110ppm and was almost independent of excess air. They therefore concluded that the introduction of vinasse makes the complete combustion of #6 fuel oil more difficult due to the possibility of formation of oil-water emulsion.

The Swedish Alpha-Laval reported the economical, technical and commercial feasibility of 60% solids vinasse combustion using swirl combustion technology [Nilsson, 1981]. In a later study, Hollandse Constructive group, A Dutch Company reported the complete combustion of 60% solids vinasse using swirl combustion technology in a specially designed steam generator [spruytenburg, 1982]. However, they did not provide technical information on the combustion of vinasse, in detail.

Table 2.18: Shepherd oil distillery Vinasse composition

	As received	Dry basis
Solids (%)	29.79	n.a.
Ash (%)	13.31	18.95
Sulphur (%)	0.08	0.12
Volatile matter (%)	48.67	69.31
Fixed carbon (%)	8.24	11.73
Carbon (%)	n.a.	39.72
Hydrogen (%)	n.a.	8.60
Nitrogen (%)	n.a.	1.65

Chakrabarty, (1964) observed vigorous foaming during concentration of vinasse from 9% to 75%. Moreover, concentration of vinasse above 75% solids resulted in crystallisation of potassium and other salts. As soon as liquid started cooling, pumping was difficult.

The dry solids of vinasse have a minimum calorific value of 6000 BTU/lb (13.9 MJ/kg). Chakrabarty (1964) incinerated vinasse by spraying in to the top of an incinerator and the ash thus produced was leached and processed to crystallise potash as KCl and K_2SO_4. Chakrabarty also found that the combustion temperature was much lower than that could be achieved in a bituminous coal fired boiler and concluded that vinasse was only suitable for a waste heat boiler to raise low pressure steam.

SAACKE delivered a plant in the 1990s to a German chemical factory for a liquid waste fuel similar to vinasse. It has 10 SAACKE SSB-burners, each of 1000 kg/h fuel feed with 10 MJ/kg LHV. Optimum combustion and low emissions can be achieved at all loads by proper split of main and core air. Strong swirling of the combustion air causes intense mixing of fuel gas and air which provides safe ignition of the blend and total burn out with homogeneous temperature profile. The plant is running with less than 10% support fuel. In 2006 SAACKE installed two more SSB-burners of 26 MW each and one with 30 MW in Brazil, at two

different tube boilers, running with the support of natural gas or fuel oil (max 30%) [SAACKE, 2009].

Gupta *et al* (1968) were the first to combust vinasse in a fluidised bed. They concentrated vinasse to 30 – 40 °Brix and burnt the vinasse in a fluidised bed at 700 °C by spraying it from the top by a spray nozzle using cold compressed air. Hot flue gas, rich in excess air, from a coke fired furnace was forced through the fluidised bed furnace to burn the sprayed vinasse. Kujala *et al.* (1976) investigated and evaluated various options for vinasse use including evaporation and fluidised bed incineration for crude potash production and ash treatment for refined potassium salt production. They have pointed out that due to low melting temperature of inorganic salts the combustion temperature is limited to below 750 °C. The real vinasse ash contains a blend of alkali salts with a melting point normally below 700 °C. Thus the combustion temperature in a fluidised bed burning vinasse needs to be below 700 °C to prevent fusion of ash. However, at such a low temperature complete combustion of volatiles is a problem. In order to deal with this issue they proposed to use a fluidised bed reactor as a gasifier and perform the after burning in a waste heat boiler. The crude potash recovered from the ash, separated by a cyclone, should have 40% K_2O, 10% CaO, 19% SiO_2 and 31% others. The potassium salts expressed as a percentage of ash should be in the following order of composition: K_2SO_4 56%, KCl 7% and K_2CO_3 5%. This crude potash containing 65 – 70% potassium slats can be used as a fertilizer. The ash thus produced can be further processed by multistage leaching, filtering and neutralising with controlled injection of H_2SO_4 to convert carbonates to sulphates, evaporation and crystallisation. The finished product thus obtained at 92% dry solids should have 83% K_2O_4, 9% KCl (traces of sodium salt) and 8% moisture.

Basic research has been carried out by Cortez and Perez (1997), who have experimented with incineration of pure and vinasse emulsions blended with heavy oils, as mentioned earlier. Although vinasse incineration technology was already presented as being commercially viable in the early 1980s by some companies, e.g., Alfa Laval and Hollandase Constructive Group (HCG), in practice, it failed to live up to expectations. From the year 1950 onwards, the firm HCG installed boilers with special furnaces to burn concentrated vinasse in Holland, Czechoslovakia and Thailand. One such plant is still working successfully in the Banghikhan distillery in Thailand [Seebaluck, *et al.* 2008].

A project, started in 2003, for electricity generation from vinasse at Mumias Sugar Company Limited (Kenya) is being carried out. Vinasse concentrated to 60% solids (wt/wt) along with bagasse will be fired in a specially designed boiler to produce 22 tonne of steam per hour at 45 bara and 400 ^{0}C. The boiler will consume 7.54 tonne per hour (TPH) of concentrated vinasse with 60% (wt/wt) solids. The boiler will use a special design traveling grate Indian technology, and will burn mainly bagasse on the grate while the concentrated Vinasse will be sprayed inside the furnace at a height of about 10 meters above the traveling grate to ensure that all the Vinasse particles burn off in suspension. The steam raised in the boiler is then expanded through a turbo-generator to generate electricity. The electricity generating section will consist of a 2.1 MW back pressure turbo-generator with the inlet steam at 40 bara and 398 ^{0}C. The steam exhausted at 5 bara will be used in the distillery and for the concentration of Vinasse [UNFCCC, 2011].

2.10.3 Raffinate:

A further biomass material as a result of the sugar producing industry which received limited attention by researchers is known as raffinate. Raffinate is similar to vinasse but with different properties depending upon the process of production. Raffinate analyses from British Sugar plc are given in Table 2.19.

Raffinate is a product of downstream process as compared to vinasse. According to British Sugar data raffinate and vainasse have very different compositions and thus expected to behave differently during combustion. Raffinate has little bit lower water content than vinasse but ash content of raffinate is higher than that of vinasse. Raffinate has higher alkaline content (calcium, potassium and sodium) but lower sulphur and nitrogen content than vinasse. As alkalis are thought to be responsible for agglomeration in fluidised bed combustion, this shows that raffinate has higher agglomeration tendency during combustion in a fluidised bed. However, due to higher potassium, calcium and phosphorous content, raffinate could be of a better economical value in terms of salts recovery by incineration and using those salts as a fertilizer.

Table 2.19: Raffinate analysis [British Sugar]

Proximate and Ultimate analysis	**Pattinson & Stead**	**TES Bretby**
Moisture (wt/wt %)	37.22	45.90
Ash (wt/wt%)	16.44	6.90
Volatile matter (wt/wt%)	44.24	39.20
Nitrogen (wt/wt%)	1.7	1.82
Sulphur (wt/wt%)	0.69	0.13
Chlorine (wt/wt%)	0.94	0.19
Sodium (wt/wt%)	0.23	917 ppm
Potassium (wt/wt%)	0.68	2760 ppm
Calcium (wt/wt%)	0.002	67000 ppm
SO_3(wt/wt%)	1.4	22400 ppm
Characteristics		
Gross Calorific value	6.28	7.02
Net Calorific value	4.86	5.49
Density kg/m^3	1330	1320
Kinematic viscosity,100 °C (cSt)	2.5	3
Dynamic viscosity (kg/m.s)	0.003325	0.00396

2.10.4 Sugar Beet Pulp:

Sugar beet pulp (SBP) is a well known potential source of cellulose. Theyield of cellulose ranges from 17 to 32% [Hasan and Nurhan, 1994]. Sugar beet pulp consists roughly of one third cellulose, one third pectin and one third hemicelluloses [Thibault *et al*, 1994]. Beet pulp can be dried pulp (90% dry matter) or overpressed pulp (greater than 25% dry matter). SBP can be used for cattle feed, feedstock for methanol production, paper production (filler) and energy recovery [Vaccari, *et al.*, 2005]. Good quality paper can be obtained by using up to 33% of wastes coming from sugar factories [Vaccari, *et al.* 1997]. Taking into account that a sugar factory processing 10,000 tonnes of beet per day uses every year about 400 tonnes of paper for packaging and 5 tonnes of paper for printing and writing, a considerable portion of

pulp and carbonation sludge can be reutilised for the production of paper for in-use [Vaccari, *et al.* 2005].

Due to its composition sugar beet pulp is considered as foodstuff [Bach Knudsen, 1997] and therefore used as food complement to animal feeds. However due to the high cost of drying and low protein content [Rouilly *et al.* 2006a] it is sometimes not economical. It is also used as a source of fibre in the composition of biodegradable materials [Turbaux, 1997] and for paper manufacturing [Wong and Breloga, 1997]. Efforts have also been made to use it in the packaging manufacturing [Rouilly, *et al.* 2006a] and to improve its nutritional properties [Ralet *et al.* 1991].

Sugar beet factories, in contrast to cane sugar which are self sustaining in energy supply by burning bagasse, need a high input of fossil energy, about 170 – 330 kWh to process one ton of beets. This is excluding the energy required to dry sugar beet pulp which takes up to one third of the whole energy demand for sugar production [Brooks *et al.* 2008]. In order to reduce external energy demand in beet sugar factories it is required to generate energy from internal sources. Few efforts have been made to produce biogas by anaerobic treatment of sugar beet pulp e.g. Stoppock and Buchholz (1985), Hutnan *et al.* (2000), Hutnan *et al.* (2001) and Brooks *et al.* (2008). According to Hutnan *et al.* (2001) energy produced in anaerobic treatment of sugar beet pulp can cover about 30.4% of the daily energy consumption of a beet sugar factory. However, Brooks *et al.* (2008) claimed a higher figure and quoted that the biogas produced could substitute about 40% of the natural gas required for thermal energy supply.

Devrim (2008) investigated the pyrolysis kinetics of the Yeni Çeltek lignite and sugar beet pulp blends prepared at different ratios (100:0, 80:20, 60:40, 40:60, 20:80, and 0:100) by thermogravimetric analysis in nitrogen atmosphere under non-isothermal conditions with a heating rate range of 30 K/min in the pyrolysis temperature interval of 298 – 1,173 K. Apparent activation energies of the lignite and sugar beet pulp were calculated as 51.55 kJ/mol and 97.27 kJ/mol, respectively. Activation energies of the blends were also calculated and were found to vary between 54.87 and 74.83 kJ/mol. Relative volatile matter yields of the blends decreased with increase in lignite to SBP blending ratio.

Yilgin *et al.* (2010) studied co-pyrolysis of 50/50 (wt/wt%) pellets of Soma Lignite and sugar beet pulp (from a sugar plant in Elazig, Turkey) at 600 °C. The pulp was dried in an oven at 50 °C until the desired moisture content of <10%, grinded and sieved to get a particle size of -100 + 200 mesh. Pellets of approximately 13mm diameter and 6 mm height were produced for pyrolysis by compaction under a hydraulic press applying a pressure of 10^4 kg_f/cm^2. By Thermogravimetric analysis (TGA) analysis they have shown that the SBP decomposes faster and undergoes higher weight loss than the lignite due to higher volatiles and lower fixed carbon content of SBP. Weight loss of SBP exceeded 90% as compared to 46% for the lignite over the heating period ending at 900 °C. Results of pyrolysis have shown that SBP given higher yields of liquid and gas and lower char as compared to lignite, see Figure 2.11. One very interesting conclusion they made, by comparing the results with expected value, that SBP and lignite behave independently in the blend and the interactions among the evolving structures are not considerable enough to be effective on the yields.

Combustion of sugar beet pulp has received very little attention. Jevic *et al.* (2007) performed basic assessment of thermal efficiency and emissions parameters by combusting 65mm briquettes of blend of wheat straw and 15% sugar beet pulp (wt/wt) in a 8kW nominal heat output prototype of combustion accumulation stove SK-2 with upper after burning.

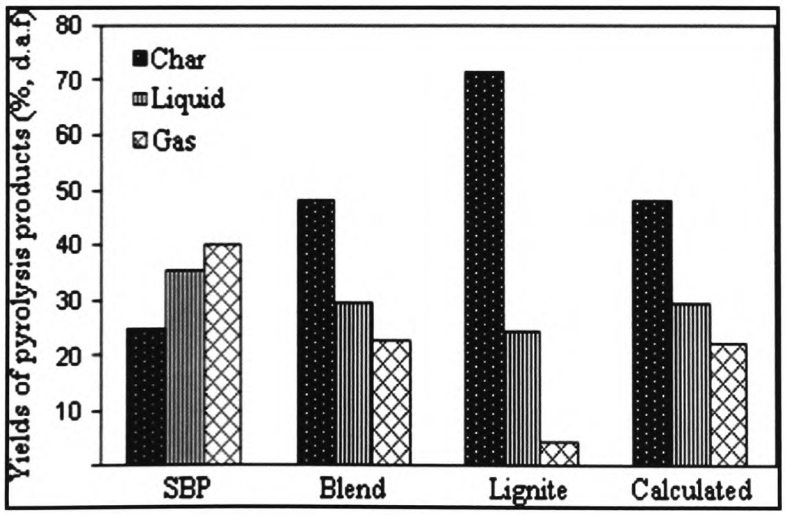


Figure 2.11: Pyrolysis yields of Sugar Beet Pulp and Lignite and their 50/50 blend [Yiglin *et al.* 2010]

Table 2.20: Characteristics of wheat straw and 15% sugar beet pulp briquettes (wt/wt)

	Wheat straw and 15% SBP*	SBP from British Sugar
Total Moisture (%)	6.34	71
Volatile matter (%)	72.15	12.9
Fixed Carbon (%)	-	14.1
Ash (%)	6.42	2
Carbon (%)	42.61	14.1
Hydrogen (%)	5.41	1.8
Nitrogen (%)	0.53	0.14
Sulphur (%)	0.05	0.14
Oxygen (%)	37.22	10.9
Sodium (%)	-	0.1
Potassium (%)	-	0.75
Calcium (%)	-	1.2
Gross CV (MJ/kg)	16.62	5.2
Net CV (MJ/kg)	15.03	3.2

*Jevic *et al.* (2007)

Characteristics of the blend are given in Table 2.20. About 12 kg of the blended fuel was combusted for a period of 40 – 70 minutes. They found that the so-called self defined thermal-technical efficiency was higher than 70% and the emissions of NO_x (corrected to 11% O_2) were around 180 mg/Nm^3.

Hrdlickaand Dlouhy(2002) co-fired lignite and sugar beet pulp having 79.7% moisture, 1.21% ash and with energy value of 1.45 MJ/kg. Combustion of pulp alone was possible when moisture content of the pulp was reduced to 45%, its energy value increased to 8.5 MJ/kg. They co-fired lignite and pulp blends in 2MW fluidised bed boiler with lignite to pulp ratios of 3:1 and 1:1. The test data is shown in Table 2.21. The data shows that at higher proportion of pulp in the blend CO emissions are higher but NO_x emissions are lower. They stated that burning of pulp can cover 30 – 50% of heat and power requirements of sugar mill. Moreover, co-firing reduces emissions of NO_x and SO_2.

Table 2.21: Measurements on FK 2MW boiler Co-Firing Lignite and Sugar Beet Pulp

Blending ratio (lignite/pulp)	3:1	1:1
Output (kW)	1100	1200
O_2 (%)	9.2	8.6
CO (mg/Nm^3) corrected to 6% O_2	111	196
Excess air	1.78	1.7
NO_x (mg/Nm^3) corrected to 6% O_2	616	570
Bed temperature (°C)	835	845

Apart from Jevic *et al* (2007) described above, there is no authentic open literature on the combustion of pressed pulp primarily due to the reason that so far the pulp has been used as a feedstock for animals. British Sugar dries pressed pulp for use as cattle feed primarily using a coal fired fluidised bed to produce hot combustion products which are subsequently fed into a rotary drier. Unfortunately the output of the fluidised bed is insufficient so that a very expensive secondary heavy fuel oil drier is also employed. Consequently there is an interest in co-firing pressed pulp with coal to increase the output of the main drying plant. There is a lack of published data on co-firing of these two fuels in a fluidised bed so that this forms a major aspect of the experimental work in this thesis.

2.11 Conclusions:

The above discussion shows that firing and co-firing of particularly high moisture, low CV biomass, can be a challenge and needs a significant effort to overcome problems posed by these materials including flame stability, low temperatures and combustion efficiency, enhanced emissions and limitations on the proportion of biomass. While co-firing of biomass has been studied on a laboratory and pilot scale, full scale trials are limited. Moreover there is little work done on the co-combustion of sugar industry by-products which are produced in huge amounts throughout the world. Therefore, the present work in this thesis focuses on the optimisation of co-combustion of pressed sugar beet pulp and to a lesser extent vinasse and raffinate with bituminous coal in a 25kW bubbling fluidised bed combustion system.

Chapter 3

Experimental Facilities and Details of the Fuels Studied in the Combustion Tests

3.1 Introduction:

As mentioned earlier in chapter 1 the current project was carried out in collaboration with British Sugar plc. and has been concerned primarily with the laboratory scale fluidised bed combustion of blends of coal with high moisture content biomass including co-products from the sugar industry such as solid pressed sugar beet pulp and raffinate and vinasse (both of which are liquids). Other biomass materials including wood pellets, and woodchips of different moisture contents were also successfully co-fired with Thoresby coal. Tests were carried out over a range of thermal inputs and excess air levels and biomass-coal blends by mass. The overall aim of the work was therefore to determine the combustion characteristics and performance of different coal-biomass blends over a range of operating conditions.

To undertake the experimental programme a laboratory scale fluidised bed combustion (FBC) test facility was designed and installed at the University of Glamorgan. The bed is 162.5 mm in diameter and is designed to operate with a maximum thermal input of approximately 25kW when fired with coal. The rig is capable of firing coal and blends of this fuel with either solid or liquid biomass. Biomass materials often have high alkali metal contents which can lead to agglomeration problems during combustion in fluidised beds. Therefore experiments are performed to see the behaviour of these materials in the bed when co-fired with coal or natural gas.

During the study it was found that pressed sugar beet pulp could be a potential fuel for co-firing with coal in the fluidised bed HGG at the Cantley site of British Sugar so that the latter stages of the project concentrated on the potential application of this solid biomass co-product. In addition to a study of the combustion characteristics of coal-pulp blends over a wide range of operating conditions, extensive bed pick up tests were performed with pressed

pulp and coal blends to see the accumulation of alkali metals in the bed under fluidised combustion conditions. The output of the full scale plant at British Sugar is limited by the flow limitations of fluidising gases. Consequently tests were also performed with water injection into the bed when firing with coal since this could be an alternative option to lower the bed temperature and hence result in an increased throughput to the HGG without the need for additional air to act as a bed coolant.

3.2 Overall Experimental set up:

The laboratory scale fluidised bed combustion system used in the present study is shown in Figure 3.1 and schematically in Figure 3.2. As can be seen the system consists essentially of an air blower which supplies the combustion or fluidising air, a natural gas burner which is largely used for startup purposes and which fires into a plenum or combustion chamber, and the fluidised bed including an overbed or freeboard section. The combustion gases are removed from the system through an exhaust section fitted with an induced draught fan. The fluidised bed is instrumented with thermocouples to measure bed and overbed temperatures and the composition of the combustion gases was measured by a portable flue gas analyser. All the measured data were automatically recorded at frequent intervals by means of a data acquisition system. A detailed description of the major components of the system is presented in the following sections and the design parameters of the rig are given in Table 3.1.

Table 3.1: Design parameters of the FBC rig

Design parameter	Basic	Ideal	Range
Gas burner firing rate (kW)	15	30	7.5 – 30
Air flow (kg/h)	40	80	20 – 80
Bed temperature (°C)	850	850	850
Fluidisation velocity (m/s)	2	4	1 – 4
Liquid biomass feeding pump flow (l/h)	6	12	0 – 12

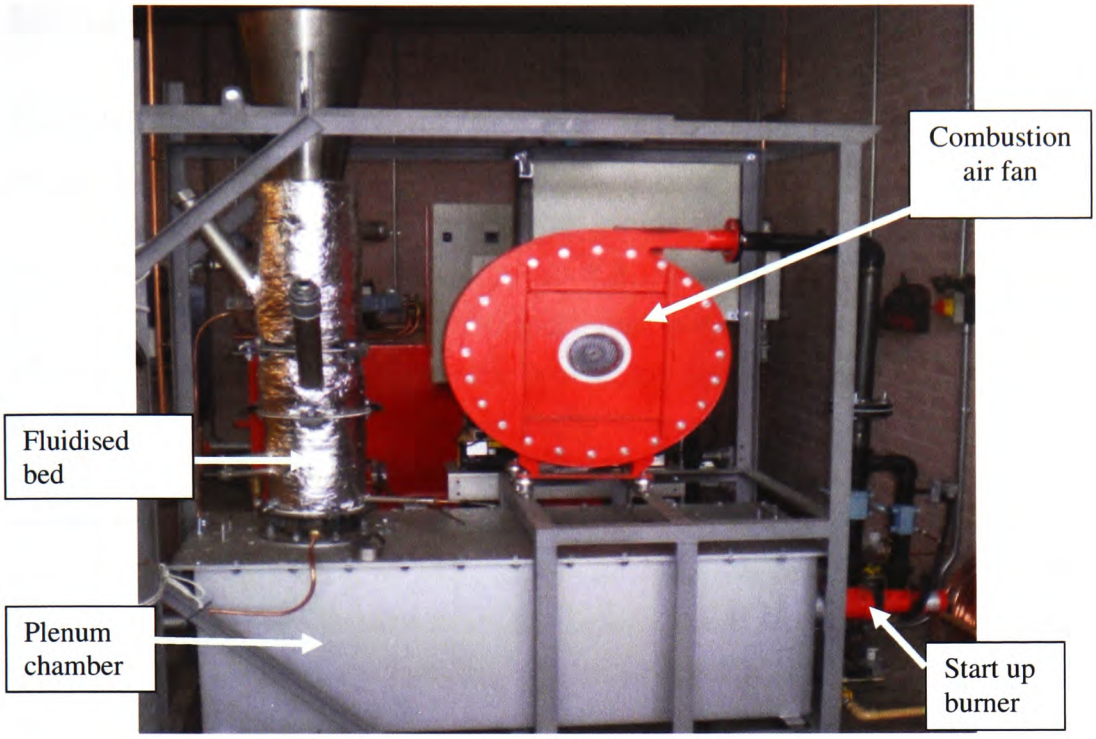


Figure 3.1: Fluidised bed combustion rig

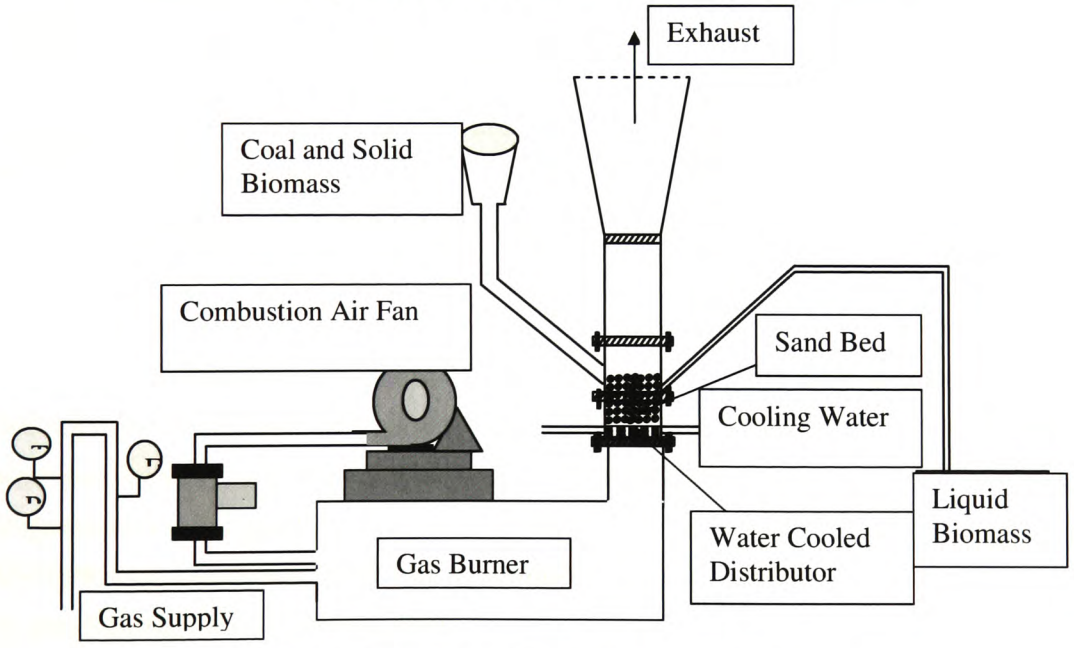


Figure 3.2: Schematic of fluidised bed combustion rig

3.2.1 Gas burner:

The natural gas burner, see Figures 3.1 & 3.3, which was primarily used for startup purposes has a maximum thermal capacity of 60 kW (double the design capacity as mentioned in Table 3.1) and fires into a combustion chamber that serves as a plenum chamber prior to the fluidised bed. The burner, manufactured by Nu Way (Model Extended MP2/6 Burner assay B32224), was capable of operating with high excess air levels to avoid excessive flame temperatures and was supplied from the natural gas supply in the laboratory which is available at 75 mbar gauge pressure. Gas supply to the burner is split into two streams, a primary gas (pilot flame) supply and a secondary gas (main flame) supply. The burner is also fitted with a pressure switch which cuts the burner off in case of excessive back pressure. The original pressure was rated at 60 mbarg which caused problem during start up in the initial tests so that it had to be replaced with a higher capacity switch, now set at 70 mbarg. Each of the two separate gas flows was controlled by solenoid valves and gas regulators fitted on the inlet pipe work. These gas flows can be controlled by screws fitted on each of the regulators. Rotating the screw clockwise, pushes it in and thus increases the gas flow by increasing the flow area.

Combustion air from the blower is measured by a turbine flow meter, manufactured by International Measurement and Control Systems (Model EA65) and is then split into primary and secondary streams which are controlled separately by manual control valves. Secondary or dilution air mixes with the main flame about 15 cm downstream of the burner outlet. In the original set up, the operation of the combustion air fan was linked to the burner i.e. once the burner is switched off, the fan is also off. This was not suitable when operating the rig with solid and liquid fuels since under these conditions it is necessary to keep the fan running when the burner is switched off. This was achieved by bypassing the burner once the bed temperature is high enough to ignite the solid fuels such as coal and other biomass in the bed. The rig is then switched to "main fuel" and burner is turned off, whilst keeping the blower on by operating the "burner bypass switch".

Overall burner operation is controlled by a control panel (Model C PNL MP2+MP6 Chamber LGB21 400/2), shown in Figure 3.4. It has switches for burner start up, shut down and reset in case of burner cut off. There are lights on the control panel which indicate the mode of

operation of the burner. During start up, the burner start up switch is pressed and the air blower is automatically switched on. Once the air flow is stabilized, the primary solenoid valve is activated and the pilot flame is ignited. After a few seconds the secondary solenoid is activated and operation of the burner is switched to main flame. If the air fuel ratio is not adequate and flame is very rich or very lean, the burner cuts off automatically. If burner is locked out the burner lockout reset button is pressed first, followed by burner stop and burner start switches to restart the burner.

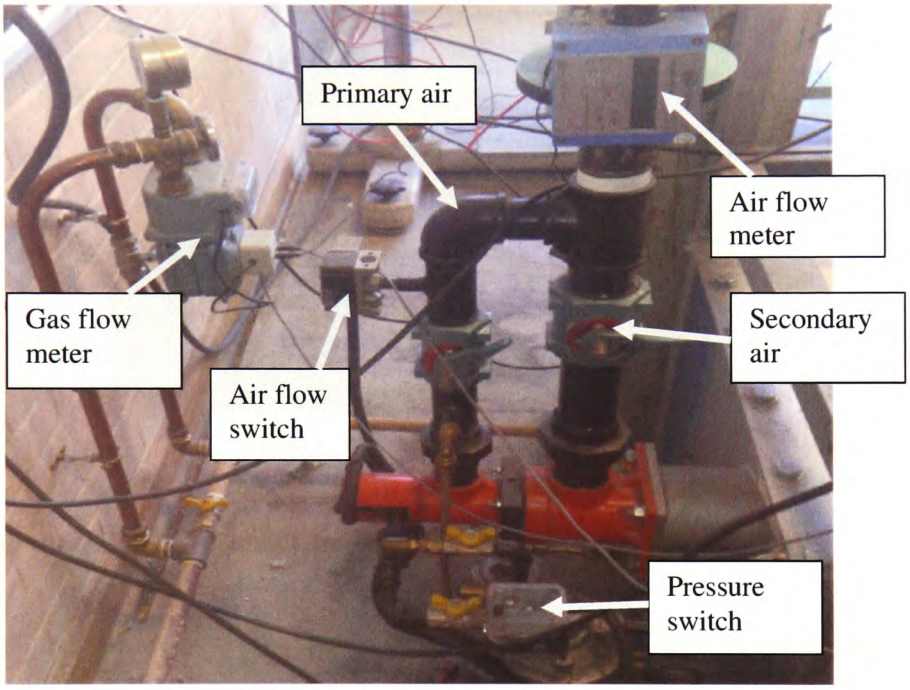


Figure 3.3: Natural gas burner

There is capability of measuring gas flow rate, temperature and pressure as well as the air flow rate. Gas flow rate is measured by a meter, EMC Euro 2000, which can measure flow rates up to 25 m^3/h. The temperature and pressure of the gas are noted manually from time to time to correct flow rate and calculate the calorific value of the gas. The air flow is measured by a turbine meter which is capable of measuring air flows from 6 to 100 m^3/h. Air flow data is logged on to a computer while the gas flow is measured manually by a calibrated pulse counting device (Hengstler, tico 731). The device is calibrated by manually measuring the metered gas flow rate over a specific period and correlating this with the number of pulses

per unit time. A calibration factor is then calculated by using the following formula and this can then be used to convert the counted pulse rate with the gas flow.

$$\text{Factor} = \frac{\qquad}{\qquad}$$

The factor was found to be 19.92.

Figure 3.4: Burner control panel

3.2.2 The Combustion or Plenum Chamber:

The burner fires into a combustion (plenum) chamber which is made of stainless steel and is 150cm long, 55cm wide and 55cm high on the outside. The chamber is internally insulated with 15cm thick Kaowool high temperature fibre insulation. The temperature of the hot gases in the combustion chamber is measured by a thermocouple which is inserted into the chamber, just below the fluidised bed distribution plate. There is also a provision for pressure measurement in the combustion chamber to monitor the back pressure exerted by the distributor plate, stand pipes and the bed material. During typical experiments the outer surface temperature of the chamber was measured at different locations to calculate the average heat loss through the chamber walls. The chamber is also equipped with a sight port situated on the end wall opposite to the burner. It is used to monitor the flame during start up and stable operation of the burner. Flue gas or air from the combustion chamber is passed through a distributor plate before fluidising the bed material.

3.2.3 The Fluidised Bed and Freeboard section:

The fluidised bed is contained in a cylindrical stainless steel tube which is externally insulated with 100mm thick Kaowool blanket to reduce heat losses to the surrounding atmosphere. The fluidising gases (either flue gas during start up or air during normal operation) from the plenum chamber enters the fluidised bed through a water cooled distribution plate having four standpipes for even distribution of the gas. The stand pipes, shown in Figure 3.5, are made of Sandvik steel 253MA (21% Cr, 11%Ni stainless steel tube) and are 89 mm long and 30 mm in diameter. Each stand pipe has 39 holes, each with a diameter of 3.5 mm, arranged in three rows.

The stand pipes are arranged on a square pitch and are equally spaced to get an even air distribution throughout the bed. The lower ends of the stand pipes are insulated with ceramic fibre to limit the heat transfer to the distribution plate.

Figure 3.5: Arrangement of the stand pipes in the distributor plate

The total length of the bed "containment tube" including the freeboard section is 1.5 m. The lower 1m high cylindrical section has a diameter of 162.5 mm while the upper conical part gradually increases to a diameter of 300 mm. The wall thickness of the lower cylindrical section is 6mm and that of the upper conical section is 3mm. The tube is separated into three sections joined together by flanges for easy dismantling for sampling of the bed material and replacing the bed in case of agglomeration and sintering problems. The height of the first flange is 305 mm and that of the second flange is 508 mm from the distribution plate. The

bed contains approximately 5 litres of sand (supplied by Garside sands) and is sized according to BS10/18 (0.85 mm to 1.7 mm with a smd of around 1.2 mm, which corresponds to a minimum fluidising velocity of 0.5 m/s at 850 °C). The resultant height of the bed above the standpipes is approximately 200 mm.

Thermocouples are installed to measure the in-bed and over-bed temperatures. The bed thermocouple is positioned 95 mm above the top of the stand pipes, i.e at about mid bed height. The freeboard thermocouples are positioned about 240 mm and 530 mm above the static bed. The bed pressure drop is measured at the bottom of the bed against atmospheric pressure by a micro-manometer (Model FC 011 Furness Controls Ltd, UK) with a resolution of 0.01 mm water gauge. The bed depth is monitored by bed pressure and a 20 cm deep bed gives a pressure of approximately 220 mm water g. Bed pressure is also monitored as an indicator of the onset of agglomeration phenomenon in the bed. A sight port is also provided to monitor the bed during the experiments. There are ports in the tube for inserting the flue gas analyzer probe. There are also arrangements for solid and liquid fuels entry into the containment tube/bed.

To avoid overheating particularly during start up with the gas burner the distributor plate is water cooled. The cooling water flow to the plate and its rise in temperature is monitored to calculate the heat losses. An interlock system is provided to shut the burner off in case of excessively high water temperature and/or low flow of the cooling water during start up. Currently the interlock temperature is set at 70 °C and if the cooling water temperature exceeds this set point, the burner is switched off automatically. A flow switch is also provided as a safety measure on the inlet of the cooling water. It prevents the burner from being fired in the case of lack of water flow through the line. The cooling water flow rate is monitored on a rotameter. During start up, the water flow is opened so that float of the rotameter is lifted to its maximum level to actuate the flow switch. Once the switch is activated the flow is reduced. A minimum water flow of 2.5 l/min also should be maintained through the flow switch and if the flow is reduced below this value, the burner will not ignite.

3.2.4 Fuel feeding systems:

Continuous and consistent fuel supply was needed for the controlled operation of the system. The present study involved solid fuels as well as liquid fuels and both of the systems are discussed here in brief.

a) Solid feeding system:

A mechanical coal and solid biomass feeding system was designed, constructed and installed on the test facility to feed these materials into the above bed freeboard, see Figure 3.6 (left). The conveying system consisted essentially of a storage hopper which delivers the coal and biomass into a motor driven screw feeder. The feed rate is controlled by varying the rotational speed of the motor using a control panel. The panel has an on/off switch and a speed controller as shown in Figure 3.6 (right). The panel is also equipped with a switch, located inside the panel that can reduce the speed of the motor by half if turned off. The screw feeder was calibrated for each fuel or blend of fuels separately. The calibration is done by measuring the mass of the fuel dispensed per unit time for each controller setting. Initial calibration tests were undertaken using Thoresby singles coal which had been broken up using a jaw crusher and subsequently sieved so that the particle size ranged from 10 to 14 mm. This range of particle size was found to be suitable for use with the feeding system and a series of 5 tests were undertaken at each motor controller setting. The measured feed rate at each setting was repeatable to within ± 6% and moreover varied linearly with the controller setting. Calibration of the screw feeder on Thoresby singles coal is shown in Figure 3.7.

Solid fuels are fed into the test rig through a a 90mm inner diameter tube which is inclined at 45° with the bed containment tube. Solid fuels are therefore fed into the freeboard about 290 mm above the top of the static bed and fall by gravity into the bed.

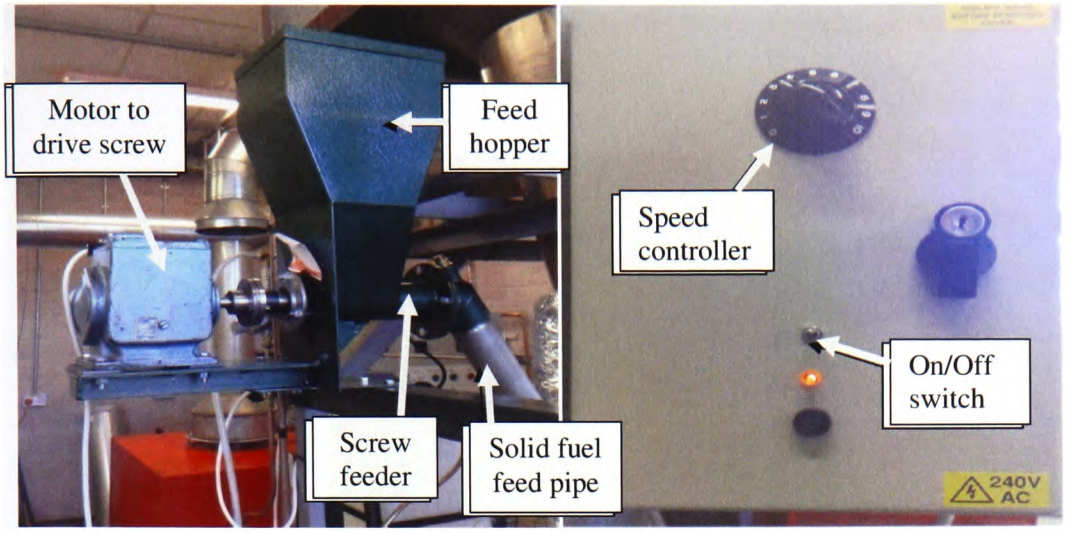


Figure 3.6: Solid feeding system

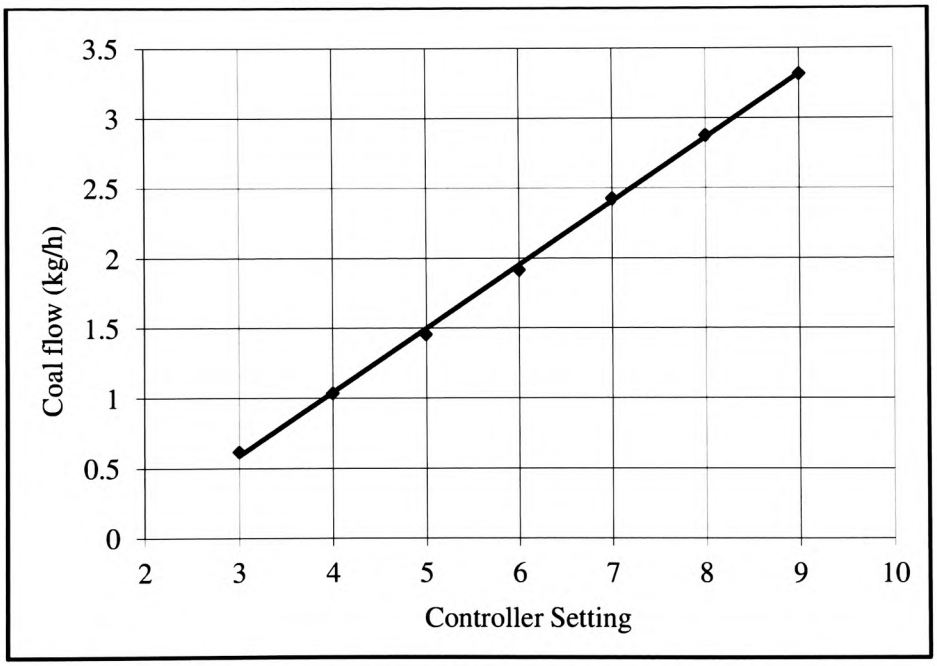


Figure 3.7: Screw conveyor calibration on Thoresby singles coal

The screw conveying system was also found to be suitable to provide a controlled feed of suitably sized wood chips and wood pellets. The pressed sugar beet pulp is much softer than these materials so that there was concern that the system would be unsuitable for this type of biomass. However preliminary tests, shown in Figure 3.8, indicated that except for possible

"bridging" problems in the hopper the system was able to successfully deliverfeed of the pressed pulp, although the flow was not consistant.

Figure 3.8: Operation of the screw feeder with Pressed Sugar Beet Pulp

b) Liquid feeding system:

As mentioned earlier, the study also potentially involves liquid fuels originating as byproducts of the sugar and alcohol industry. In order to feed these materials into the bed a liquid feeding system was installed. The feeding system, see Figure 3.9, consisted of a storage tank, a peristaltic pump, a feed pipe, and a compressed air supply. The liquid fuels were stored in the tank and pumped by the peristaltic pump into the bed through a 6 mm diameter stainless steel feed tube. The feed pipe delivers liquid biomass in to the middle of the bed (51 mm above the stand pipes) to ensure that the fuel enters a well fluidised region of the bed. The peristaltic pump is a positive displacement variable speed metering pump, EV500 model, manufactured by "Autoclude pumps" now "Verderflex" and was used to feed a measured flow rate of the liquid biomass into the bed. The maximum capacity of the pump is 185 l/min.

The pump was calibrated by relating the rotational speed of the rotor to the delivered volume. A typical linear relationship, in this case for water, is given in Figure 3.10. A compressed air supply is used to prevent the feed pipe from being blocked by the bed material and also to atomise the liquid biomass so that it is sprayed into the bed. The compressed air line is equipped with two pressure regulators installed in series. The First in the series is a Fengling

pressure regulator/pressure controller followed by Nova Comet BP1813, pressure reducer, which reduces the air pressure down to 50 – 150 mbarg. Cooling water is used to cool the feed pipe to prevent the biomass from being "coked" in the hot feed pipe. The water supply is used to flush the feed pipe at the end of the experiment after biomass feeding is stopped.

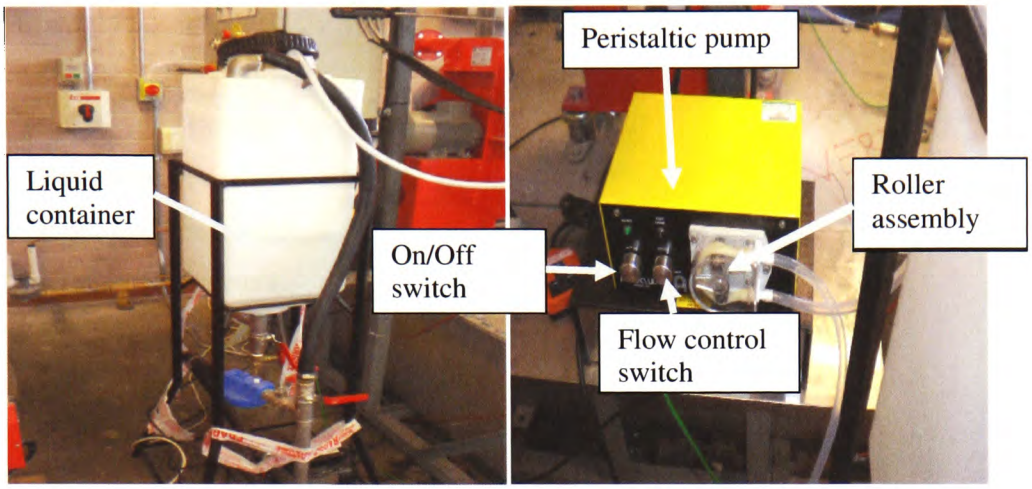


Figure 3.9: Liquid feeding system

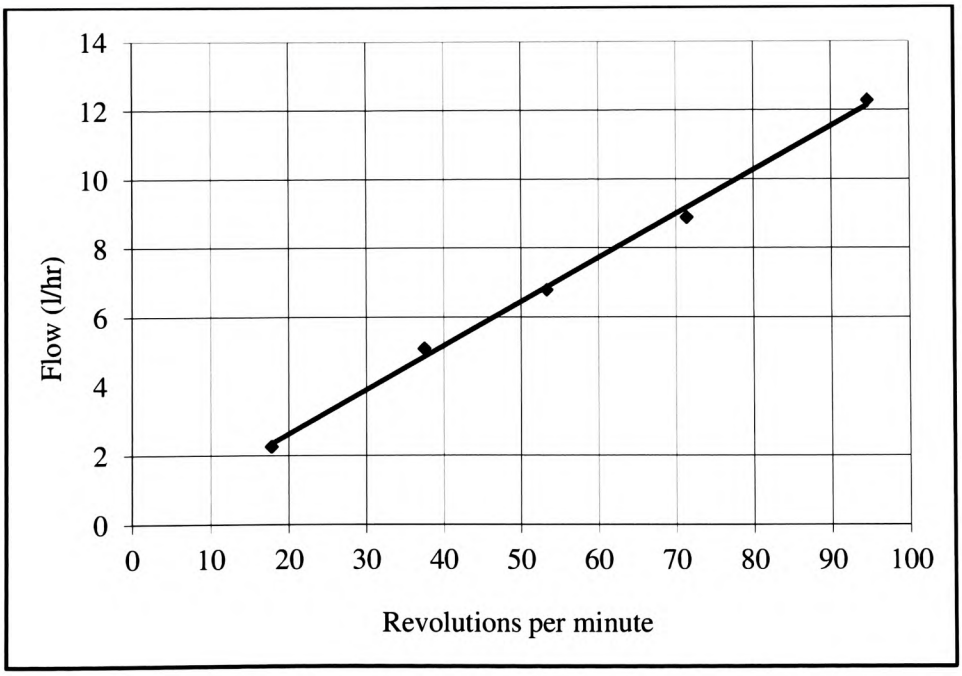


Figure 3.10: Peristaltic pump calibration

3.2.5 Data logging system:

Two computers are used to record data in the current research work. One of the machines is dedicated to record the data from the flue gas analyzer, Figure 3.11, while the other one is used to record temperature, pressure and flow measurements, Figure 3.12. Following data was logged every 10 seconds for post experiment analyses.

- Combustion chamber temperature
- Bed temperature
- Freeboard temperature
- Exhaust temperature
- Distribution plate cooling water temperature
- Air flow rate
- Bed pressure
- Flue gas composition (CO, CO_2, O_2, NO_x, SO_2)

Following parameters were measured, every 10 – 15 minutes, and noted manually during the tests.

- Natural gas flow rate
- Solid fuel flow rate
- Liquid fuel flow rate
- Cooling water flow rate

Details of the temperature, pressure and flow measurements are given elsewhere in this chapter.

3.2.6 Flue gas analyses:

In order to understand the combustion characteristics of different fuels, the flue gas was analyzed throughout the experiments and was logged on to a computer, every 10 seconds, by a system as shown in Figure 3.11. Access ports were provided in the freeboard region, to measure the composition of the exhaust gases at different heights above the bed. Generally,

however measurements were made 810 mm above the distribution plate. Two gas analyzers are used, a portable Testo 33 and a Testo 350 model. The Testo 350 is equipped with a special ceramic probe for emissions measurements in environments involving high temperatures. The analysers measure O_2, NO_x, SO_2, CO and CO_2. Testo 350 model also measures hydrogen.

Figure 3.11: Flue gas analyzer and data logging system

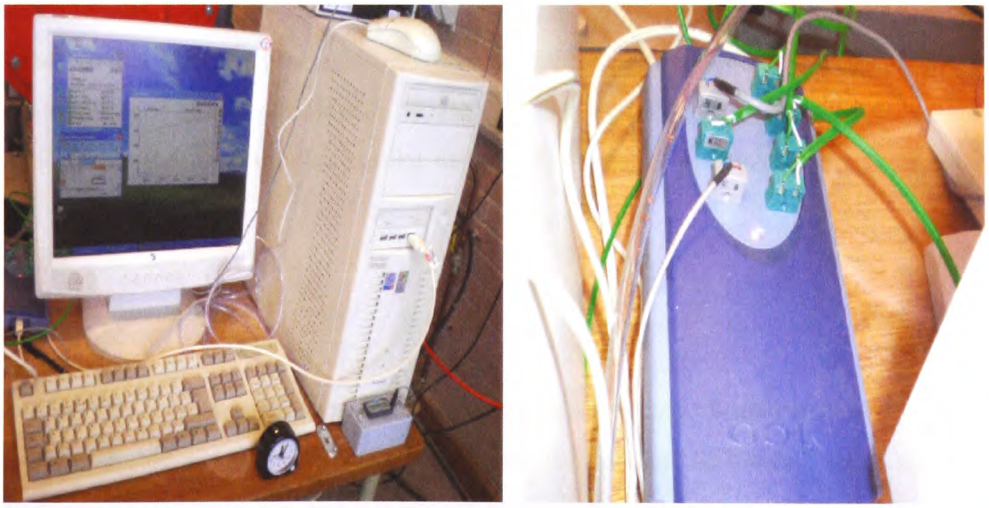


Figure 3.12: Temperature, Pressure and Flow data logging

As the study involves high moisture fuels, the flue gas can have high amounts of water in it. To ensure that the flue gas is measured on dry basis the flue gas moisture is condensed and separated before the analyzer. This is achieved by passing the flue gas sample through a coil immersed in a water bath before the analyzer. Compressed air is used, from time to time, to flush any residual water condensed in the coil.

3.2.7 The Exhaust system:

The flue gas is extracted by an exhaust fan which is capable of withstanding temperatures of up to 200 °C. As the flue gas leaving the freeboard section is at high temperature it is diluted with copious amounts of air to bring its temperature down before entering the exhaust duct. Dilution brings the flue gas temperature down to below 100 °C as monitored by a thermocouple in the exhaust ductwork.

3.3 Control and lockout systems:

In order to make the rig as safe as possible some controls and lockouts are provided. It should be noted, however, that these lock outs are linked only to the natural gas burner. When the rig is operated on the main solid or liquid fuel there is no automatic provision to cut the fuel supply off so that it is the responsibility of the operator to monitor all the parameter as closely as possible under these conditions. If any of the operating parameters are outside the "normal" limits the fuel supplies can be turned off manually to ensure the safe operation of the rig.

3.3.1 Bed Temperature:

Control of the bed temperature is very important in any fluidised bed system. Bed temperature should not be lower than the ignition temperature of the fuel since unburnt fuel will start accumulating in the bed. On the other hand the temperature should not be too high to avoid damage to the bed containment tube, and distribution plate etc. In order to ensure the safety of the system, the bed temperature was restricted during start up to a maximum temperature of 920 °C. As long as the temperature is below this limit, operation of the rig is thought to be safe. Once this temperature is exceeded, the gas burner is automatically shut

down by a thermostat, shown in Figure 3.13. This prevents the temperature of the bed from rising any further and ensures the safe operation of the rig.

3.3.2 Cooling water temperature:

Cooling water is provided to the distribution plate to prevent its excessive overheating. In order to control the temperature of the distribution plate, temperature of the distribution plate cooling water is monitored continuously. The temperature is controlled by the same thermostat as is used for controlling the bed temperature. The temperature of the cooling water is set to a maximum value of 70 °C, above which thermostat, shown in Figure 3.13, cuts the burner off for safe operation of the system.

3.3.3 Cooling water flow control:

A second level of safety to avoid overheating of the distribution plate is provided by interlocking the flow of water with the operation of the burner. The Flow of the cooling water is monitored continuously during the tests. A flow switch, shown in Figure 3.14, is provided on the water flow line. If water flow is reduced below acceptable limits during operation of the rig, the switch cuts the burner off to protect the distribution plate from being damaged by overheating.

3.3.4 Pressure switch:

During start up from cold as mentioned earlier, the hot gases from the combustion chamber pass through a set of stand pipes prior to fluidising the bed. The Resistance of the stand pipes and bed material exerts a back pressure on the system. A pressure switch, see Figure 3.3, is provided on the burner which cuts the burner off if the back pressure exceeds a set value. The pressure switch is now set at 70 mbarg.

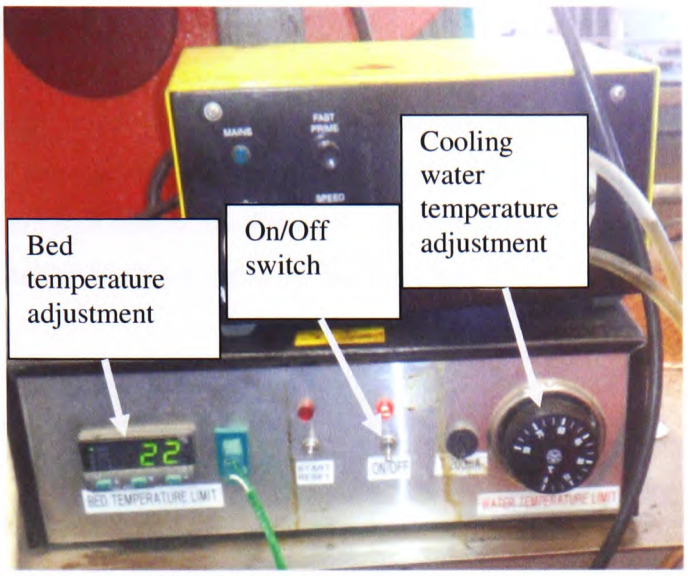


Figure 3.13: Thermostat for bed temperature and cooling water temperature limits

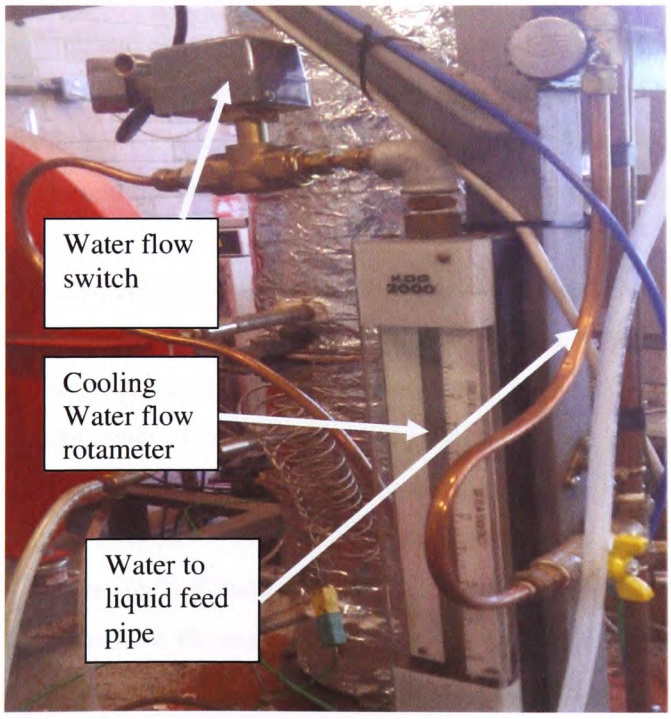


Figure 3.14: Water system for cooling distribution plate and bed injection

3.3.5 The Air flow switch:

Without sufficient air, burner will not fire and natural gas will accumulate in the combustion chamber and thus pose an explosion risk. In order to make sure that the operation of the burner is safe, an air flow switch, see figure 3, is provided on the primary air flow line. The switch acts as a safety feature to turn off the gas flow if for any reason the air flow is switched off.

3.3.6 Emergency switch:

As an overall safety control an emergency switch is provided to cut the burner off in case of malfunction of any of the equipment. The switch is located on the main panel alongside burner start, burner stop and burner lockout reset switches, see Figure 3.4.

3.4 Details of the Fuels and Combustion tests:

After pre-commissioning, and also to gain experience on operation of the facility, the rig was characterized on natural gas. Typical composition and properties of the natural gas are given in Table B1 in Appendix B. During these experiments the air flow was varied to change excess O_2 in the flue gas and the natural gas flow was varied to change thermal input.

Preliminary tests were also undertaken with emulsions of oil and water to simulate firing of a high moisture content liquid fuel. Again the main purpose was to gain experience in the operation of the fluidised bed. After initial testing on natural gas and the oil-water emulsion, tests were then undertaken with Thoresby coal and then with this coal co-fired with a range of biomass materials including wood chips, wood pellets, and pressed sugar beet pulp. In addition as described in Chapter 7 which covers agglomeration two other sugar industry liquid co-products vinasse and raffinate were co-fired with coal. Some of these potential biomass fuels are byproducts of the sugar making process so that in order to understand the origin of these fuels this process is described briefly in the next section.

3.4.1 The Sugar making process:

The overall process is shown diagrammatically in Figure 3.15. Sugar beet is processed initially to remove stone and soil and the clean beet is then sliced into thin strips called cossettes. These are pumped to diffusers where they are mixed with hot water to extract sugar juice. The raw juice is then separated from the residual fibrous material which is mechanically pressed to partially remove moisture. At British Sugar's Cantley factory this so-called pressed sugar beet pulp is dried, at present, in coal and oil fired driers before being compressed into pellets which are sold in bulk as animal feed. The present project is largely concerned with co-firing of the pulp with coal to reduce the use of the expensive oil-fired driers since an economic analysis has indicated substantial financial benefits.

The raw juice is then progressively heated through complex heat recovery systems which minimize the energy demand of the plant. Milk of lime and CO_2 are added to precipitate calcium carbonate or chalk which removes the impurities in the raw juice. The extracted "thin juice" passes through multiple effect evaporators which boil the water off and produce syrup known as "thick juice". Crystallisation of sugar takes place in pans which boil the thick juice under vacuum. When the crystals are fully grown the blend of crystal sugar and syrup, known as massecuite, is spun in centrifuges to separate the sugar from the syrup or "mother liquor". After the sugar crystals are washed, dried and cooled they are conveyed to storage silos.

The syrup is further processed to produce betaine, more sugar and raffinate for animal feed. Raffinate which is also tested in this project is also known as "desugared beet molasses". A further biomass co-product also considered in this project is vinasse, a co-product from a bioethanol process. Typical analyses of these sugar industry co-products as provided by British Sugar are given in Table 3.2.

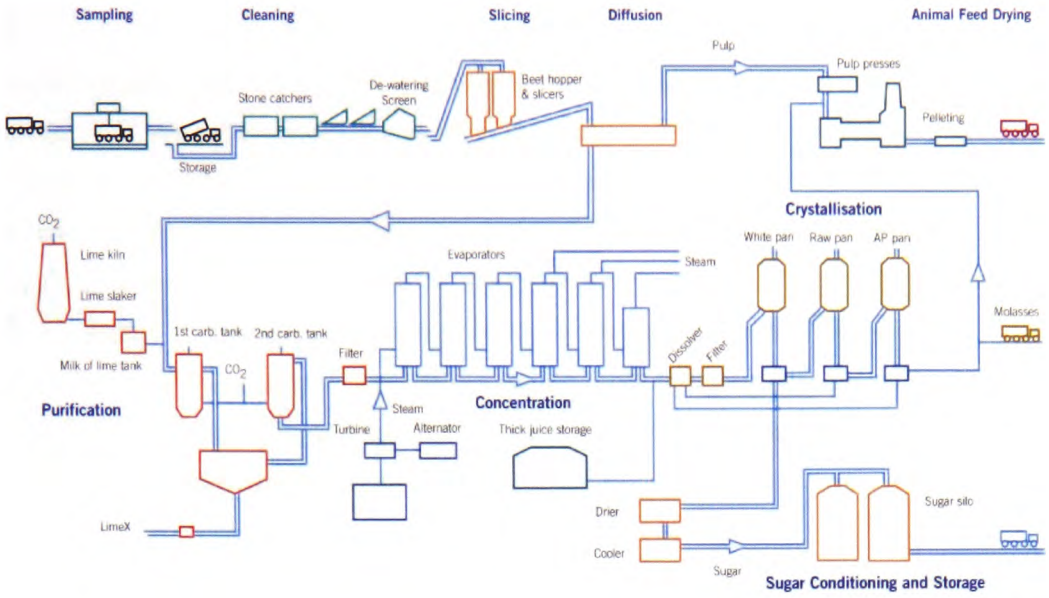


Figure 3.15: Sugar making process [British Sugar]

Table 3.2: Pressed pulp, Vinasse and Raffinate analysis [British Sugar]

	Pressed pulp	Vinasse	Raffinate
Dry solids (%)	26 – 30	40 – 45	50
Total ash (%) db	6 – 8	22 – 25	36 – 44
Sugars (%) db	1.5 – 2.2	8.7	12 – 15
Volatiles solids (%) db	92 – 94	-	-
Sulphur (%) db	0.25	5	1
Nitrogen (%)d b	1.6	5	3.2
Phosphorus (%) db	0.1	0	0.16
Potassium (%) db	0.75	7	13
Sodium (%) db	0.1	2.5	3.6
Calcium (%) db	1.2	0.05	0.76

3.4.2 Oil-water emulsion tests:

In order to gain experience in the combustion of high moisture content liquid fuels, it was decided to do some preliminary tests with an oil-water emulsion. Gas oil was used to conduct the experiments and the properties are given in Table B2 in Appendix B. The emulsion of gas oil with water was aided by adding an emulsifier, Span 80 from FLUKA, supplied by Sigma-Aldrich Company Limited. Properties of the emulsifier are given in Table B3 in Appendix B. The emulsifier is a hydrocarbon called Sorbitan Mono-oleate with the chemical formula $C_{24}H_{44}O_6$. It was found that the amount of Span 80 required for satisfactory emulsion was 5% of the total volume. This amount was thought to be sufficient to affect the combustion process thus has been accommodated in the combustion calculations.

The emulsion was introduced into the bed by the peristaltic pump though a stainless steel tube. Two compositions of the emulsion were tested. A 50/50 oil-ater emulsion was tested to simulate moisture content of the vinasse while a 30/70 oil-water emulsion was tested to simulate calorific value of the vinasse.

The procedure adopted for the tests is briefly explained here. The same procedure is applied to the feeding of other liquid biomass into the bed.The rig is fired with gas as usual. The parameters are set for a particular thermal input and excess air level. Compressed air supply is turned on to keep the feed pipe clear of any sand particles which may go into the pipe during fluidisation and possibly cause its blockage. When the bed temperature becomes stable and the rig is at steady state conditions as noted by the stable bed temperature, water supply (at very low flow) is turned on to cool the liquid feeding pipe. After few moments high moisture biomass feeding is started at a set flow rate and water supply is turned off. The effect of the high moisture biomass on bed behaviour and emissions is noted.

3.4.3 Tests with Thoresby Coal:

A series of combustion tests were undertaken on the pilot scale fluidised bed with Thoresby singles coal, supplied by British Sugar, which was then crushed and sieved, see Figure 3.16, to provide coal in the size range of 10 – 14 mm which was suitable for feeding by the screw

conveyor. Typical as received properties (proximate and ultimate analyses) of this coal, as provided by British Sugar and the BCURA Coal Bank are presented in Table 3.3.

Table 3.3: Thoresby Coal Characterisation [BCURA and British Sugar]

Ultimate analyses (as received)		Proximate analyses (as received)	
Carbon (%)	74.42	Moisture (%)	5.6
Hydrogen (%)	4.06	Ash (%)	4.9
Oxygen (%)	6.97	Volatiles (%)	34.2
Nitrogen (%)	1.62	Fixed carbon (%)	55.3
Sulphur (%)	2.01	Net CV (MJ/kg)	30.03
Chlorine (%)	0.63	Gross CV (MJ/kg)	31.04
Air/Fuel st. (kg/kg)	9.6	Density (kg/m^3)	710
Ash analyses (%)			
Na_2O	5.9	SiO_2	34.3
K_2O	1.4	SO_3	3.1
CaO	3.3	TiO_2	0.9
MgO	0.7	Mn_3O_4	<0.2
Fe_2O_3	26.3	P_2O_5	<0.2
Al_2O_3	23.8		

Figure 3.16: Crushed and sieved Thoresby singles coal

During start up the fluidised bed is preheated by the gas burner to a temperature above the coal ignition temperature before delivery of the coal into the bed. Tests with Thoresby singles coal were conducted at six different thermal inputs ranging from 8.7 to 18.2 kW based on the net calorific value of the coal. The excess air level based on the oxygen concentration in the flue gases was varied from 80 to 200%. This extensive range of tests with coal provided reliable data for comparison with the results of the co-firing tests with coal-biomass blends.

3.4.4 Co-Firing of Coal and Wood Chips:

Wood chips for preliminary tests were obtained from Wood Recycling Limited, Cardiff. However these were found to be too big for the screw feeder. Therefore, smaller sized wood chips were specially requested from South Wales Wood Recycling Ltd., Bridgend. However the smallest size of the wood chips which could be obtained from the supplier still contained a significant proportion of larger particles. Consequently it was not possible to feed this as received fuel using the existing feed mechanism since the larger chips jammed and blocked the screw feeder. The wood chips were therefore sieved in order to obtain wood chips with a size less than 10mm. A typical analysis for the wood chips is presented in Table 3.4. Table 3.5 presents typical analysis of ash from wood chips. Preliminary tests have been undertaken with a 50/50 by mass blend of coal and the wood chips in the "as received" condition with approximately 15% moisture, and also with the same blend of coal and wood chips which had been soaked in water to provide a higher moisture content of 55%. Figure 3.17 shows the original wood chips and those soaked in water to raise their moisture content. These co-firing tests were undertaken with net thermal input of 15 kW at 10.3 to 13.6% O_2 in flue gas with 15% moisture wood chips and at 9.5 to 12.9% O_2 at 55% moisture wood chips.

Table 3.4: Typical composition of as received Wood Chips

Moisture %	15	55
Carbon %	40.7	21.51
Hydrogen %	7.3	3.88
Oxygen %	31.9	16.84
Nitrogen %	0.95	0.51
Sulphur %	0.01	0
Chlorine %	0.83	0.49
Moisture %	15	55
Ash %	3.32	1.77
NCV (MJ/kg)	14.5	6.5
GCV (MJ/kg)	16.5	8.7
Air/Fuel st. (kg/kg)	5.8	3.08
Density (kg/m^3)	220	420

Table 3.5: Typical composition of ash from Wood Chips

Constituents	% of Ash	Constituents	% of Ash
P_2O_5	0.6	CaO	22.4
SiO_2	35.8	MgO	2.8
Fe_2O_3	3	Na_2O	2.4
Al_2O_3	5.3	K_2O	2.2
SO_3	15.9	TiO_2	4.1

a) Wood chips as received b) soaked in water

Figure 3.17: As received and soaked in water Wood Chips

3.4.5 Co-Firing of Coal and Wood Pellets:

The wood pellets are a prepared biomass fuel with low moisture content and a relatively high calorific value, see Table 3.6 which presents a typical analysis. Table 3.7 gives typical analysis of ash from wood pellets. Moreover this biomass material can be readily fed to the fluidised bed using the screw conveying system because of the size and consistency of the pellets. Consequently tests were undertaken when firing solely with the pellets and when they were blended as a 50/50 mix with the coal. Co-firing tests have been carried out at net power inputs from 9.6 to 12.2 kW with O_2 variations from 10.2 to 14% in the flue gas. Wood pellets for the tests were obtained from Treenergy Woodfuels Ltd., Monmouth. Figure 3.18 shows wood pellets as received and mixed with coal on 50/50 weight basis.

Table 3.6: Typical analyses of Wood Pellets

Moisture (%)	8.7	Ash (%)	0.5
Carbon (%)	45.8	Hydrogen (%)	5.5
Oxygen (%)	39.4	Nitrogen (%)	0.08
Sulphur (%)	0.01	-	-
Gross CV (MJ/kg)	18.2	Net CV (MJ/kg)	16.8
Air/Fuel st. (kg/kg)	5.4	Density (kg/m^3)	680

Table 3.7: Typical composition of ash from Wood Pellets

Constituents	% of Ash	Constituents	% of Ash
P_2O_5	3	CaO	25.2
SiO_2	16	MgO	5.5
Fe_2O_3	2.3	Na_2O	1.1
Al_2O_3	2.8	K_2O	10.5

a) Wood pellets b) 50/50 Coal-Wood pellets

Figure 3.18: Wood pellets and Coal-Pellets blend

3.4.6 Co-Firing of Coal with Pressed Sugar Beet Pulp

A preliminary economic analysis carried out by British Sugar has indicated that there are financial benefits in co-firing pressed sugar beet pulp on their coal-fired fluidised bed hot gas pulp drier. This arises because it would no longer be necessary to use expensive oil-fired system to dry additional pulp. Consequently particular attention was paid to co-firing of this biomass material in this project. Pressed sugar beet pulp has a very high moisture content of approximately 71% and very low CV of 3.2 MJ/kg (net), see Table 3.8, and so cannot be burnt without a support fuel. Consequently tests were undertaken with coal-pulp blends in the mass ratio 70/30, 60/40 and 50/50. It was not possible to achieve stable combustion if the proportion of pressed pulp was increased above 50%. Figure 3.19 shows pressed pulp as received and mixed with coal on 50/50 weight basis. The very low density of the pulp results

in very low amount of coal on a volume basis so that the blend is a large volume of pulp surrounding a few discrete pieces of coal. This would result in fuel feeding problems on the full scale plant but nevertheless it was considered that the combustion characteristics of blends of pulp and coal should be extensively studied. Therefore tests were undertaken with net thermal inputs ranging from 11.8 to 22.8 kW and the oxygen content of the combustion products was varied from 5.1 to 13.3% during the tests.

In addition to the combustion tests further work was undertaken to investigate potential problems with bed agglomeration when firing pressed pulp. In addition agglomeration or bed clinkering was also studied when co-firing coal with raffinate or vinasse. This work is described in Chapter 7 so no further details are presented at this stage.

Table 3.8: Composition of Pressed Sugar Beet Pulp on as received basis

Moisture (%)	71.0	Ash (%)	2.0
Carbon (%)	14.1	Hydrogen (%)	1.8
Oxygen (%)	10.9	Nitrogen (%)	0.14
Sulphur (%)	0.14	-	-
Gross CV (MJ/kg)	5.2	Net CV (MJ/kg)	3.2
Air/Fuel st. (kg/kg)	1.8	Density (kg/m^3)	480

a) Pressed Pulp b) 50/50 Pulp-Thoresby coal blend

Figure 3.19: Pressed Pulp and Coal-Pulp blend

3.5 Water Injection Tests:

One of the main affects of co-firing with pressed pulp is that the moisture in the pulp cools the bed so that a specified bed temperature can be achieved with a lower air flow rate. This cooling effect would enable a higher thermal rating to be achieved on the full scale plant at British Sugar, Cantley since the amount of coal which can be burnt is currently restricted by limitations in the supply of fluidising gases or air. A simpler and consequently cheaper method of cooling the bed could be the direct injection of water into the bed. However there are concerns that this could result in excessive generation of carbon monoxide through a water gas reaction. Consequently tests were undertaken to determine the affects of water injection into the pilot scale fluidised bed when firing Thoresby coal. The first set of tests involved injection of a high water flow of 11 l/hr into the bed which was initially stabilised at 900 °C. Under these conditions the bed temperature gradually decreased, until the water was switched off and the bed temperature increased again. Further tests were carried out under steady state conditions in which the coal, water and air flows were varied. An attempt is made to calculate the effect of water injection on the reduction of air flow and thus increased coal input.

Chapter 4

Results and Discussion of the Initial Combustion Tests

4.1 Introduction:

This chapter and the following (Chapter 5) contain the results of the experiments carried out on the Fluidised bed combustion rig with different fuels. Preliminary testing and commissioning has been carried out with natural gas and oil-water emulsions. Subsequently, wood pellets, wood chips with different moisture contents and pressed pulp have been fired and/or co-fired with Thoresby coal at different power inputs and excess air levels. This chapter presents commissioning and characterisation of the rig on natural gas and preliminary tests of co-firing natural gas and gas oil and water-gas oil emulsions. Bed and freeboard temperature, energy balance and efficiency data of the tests is presented and discussed in this chapter. Co-firing tests of wood pellets, wood chips and pressed sugar beet pulp with Thoresby coal are presented in Chapter 5.

4.2 Energy balance Calculations:

To calculate the combustion efficiency energy balance calculations have been performed on the basis of the experimental data obtained from the fluidised bed rig firing different fuels either alone or in co-combustion with coal. The distribution of energy is characterised into flue gas heat content, heat loss to the distributor cooling water, heat loss through the walls of the rig including the walls of the combustion chamber as well as the containment tube.

4.2.1 Energy balance and Characterisation on Natural Gas:

As it has been stated earlier, the rig was initially characterised on natural gas. Tests have been carried out at net thermal inputs ranging from approximately 30 to 40 kW at different excess

oxygen levels in the flue gas ranging from 7.8 to 11.3% (i.e. excess air levels ranging approximately 60% to 120 %). The tests were aimed at getting a stable bed temperature at any set conditions.

Bed temperatures for the natural gas tests (as measured by a thermocouple inserted into the middle of the static bed) as a function of thermal input at different excess air levels is plotted in Figure 4.1. The figure shows that the bed temperature increases with increase in power input at constant O_2 concentration in the flue gas. The figure also shows that the bed temperature decreases with increase in excess air (O_2 concentration in flue gas) at constant power input. Thus, to get a particular bed temperature at a lower power input lower excess air is required. For example, to get a bed temperature of 850 °C at 30 kW, the O_2 concentration in the flue gas has to be less than 7%, which is generally too low for burning coal or biomass. Therefore to maintain the same bed temperature at higher excess air levels higher power inputs are required e.g. at 10.3% O_2 (around 87% excess air) the necessary thermal input required to get a bed temperature is 38 kW.

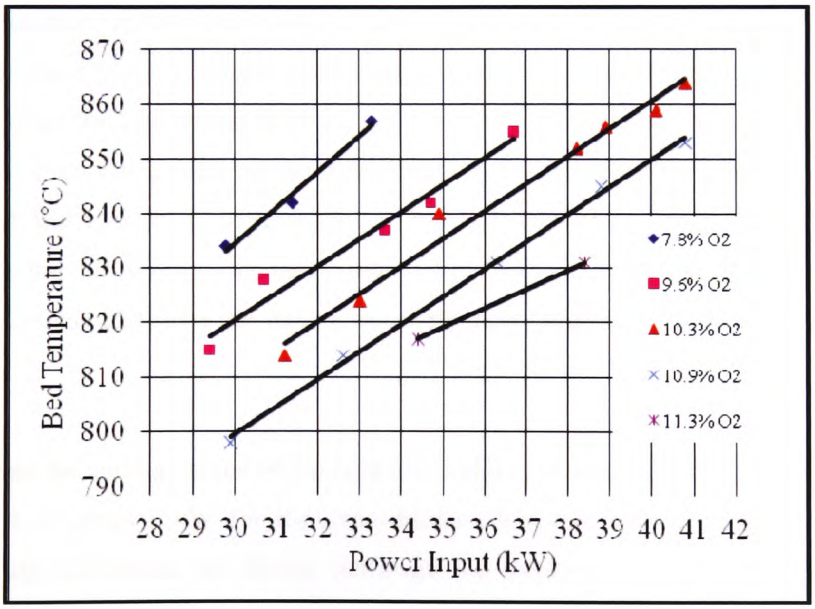


Figure 4.1: Power input vs. Bed temperature at different excess air levels for natural gas

These variations in bed temperature with power input and excess air may be due to changes in the temperatures of the combustion gases exiting the combustion chamber. Consequently,

to determine typical heat losses from the rig energy balance calculations have been performed based on the experimental natural gas test data. Where appropriate these heat losses can also be applied to the characteristics of the rig when firing other fuels. The energy balance takes into account the flue gas heat content, cooling water heat loss and heat loss through the walls of the rig which includes heat loss through the walls of the combustion chamber and the containment tube. For natural gas firing the flue gas heat content, the cooling water heat loss and the heat loss through the walls of the containment tube can all be calculated so that the combustion chamber heat loss has been determined by the difference between the thermal input and these various losses. As described in Chapter 3, the flue gas leaving the combustor is passed through the containment tube (surrounding the bed and freeboard) before going to the exhaust. The temperature of the flue gas is measured at three different points along this containment tube as shown in Figure 4.2. As mentioned previously the bed temperature (BT) is measured by a thermocouple inserted into the middle of the static bed and it is assumed that the flue gas leaving the bed is at the temperature of the bed. Two freeboard temperature measurements are taken freeboard temperature (FBT_1) at 0.24m above the bed and freeboard temperature 2 (FBT_2) at 0.53m above the bed. In the case of natural gas firing, combustion is essentially complete in the combustion/plenum chamber and combustion does not take place in the bed or above the bed. Consequently the changes in freeboard temperatures are a result of the heat losses through the walls of the containment tube. Based on these temperatures the heat content of the flue gas for all the three locations is calculated by using the specific heat capacities of the individual components of the combustion gases. Heat loss 1 (HL_1) is calculated by the difference of the heat content of the flue gas at BT and FBT_1. Similarly heat loss 2 (HL_2) is calculated by the difference of the heat content of the flue gas at FBT_1 and FBT_2.

It is found that the average value of the heat loss 1 (HL_1) is about 1.5 kW and that of the heat loss 2 (HL_2) is about 1 kW for the experiments conducted with natural gas at different thermal inputs and excess air levels. Although the losses are dependent on the flue gas temperatures, the calculated values of these heat losses did not show wide differences despite changes in flue gas flow rate as the thermal input and excess air varied throughout the tests.Therefore, it is assumed that the heat losses calculated for natural gas, HL_1 and HL_2, also apply to the combustion of other fuels. This assumption can then be used during the tests

with other fuels (such as coal, wood pellets, wood chips and pressed pulp) to estimate the combustion efficiency as well as the freeboard or over bed burning of the fuels.

The cooling water heat loss is calculated directly from the temperature difference at the inlet and outlet and the flow rate of the water flowing through the distribution plate. Initially In order to calculate heat losses through the walls of the combustion chamber, the temperatures of the walls were measured at different points. However these temperatures varied significantly from point to point with the highest temperatures around 150 °C found close to the burner and the lowest around 100 °C at the wall opposite to the burner. Therefore, it is not possible to calculate the heat loss through the combustion chamber walls by this method with the appropriate accuracy. Consequently, it is calculated by the difference of the energy input by the fuel and combustion air and the heat outputs (the heat loss to the cooling water and the heat content of the flue gases exiting at bed temperature).

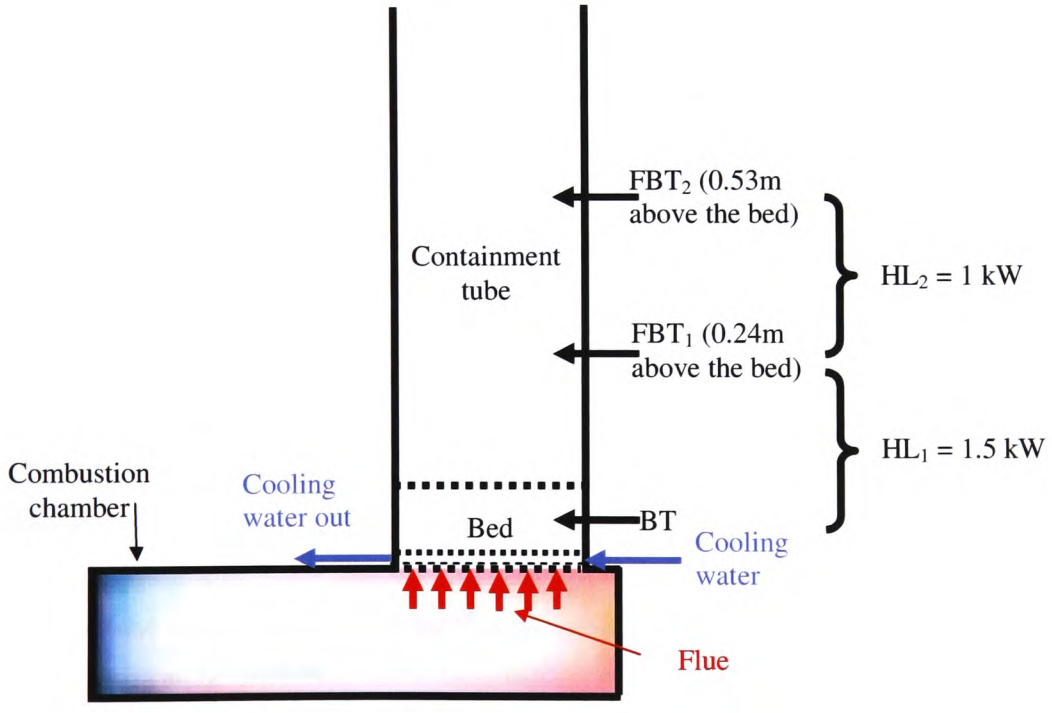


Figure 4.2: Energy Balance explaination

Distribution of energy between the cooling water, the combustion chamber and the flue gas at BT is given in Table 4.1.

Table 4.1: Distribution of heat losses from the Fluidised Bed rig

	Heat losses (%)
Combustion chamber	10.9 – 22.6
Cooling water	13.8 – 18.3
Flue gas	59.5 – 74.3

The table shows that the major proportion of the energy, about 60 to 75%, is carried by the flue gases. Heat lost to cooling water is about 14 to 18%, while that lost through the walls of the combustion chamber represents about 11 to 23% of the total energy input. The heat loss through the walls of the combustion chamber shows wider range as compared to the heat loss to cooling water although both of these are affected by total power input and thus flue gas mass flow as well as flame temperature. The difference in range could be due to considerably larger heat transfer area of the combustion chamber as compared to cooling water flow path. The difference may also be due to difference in heat transfer mechanism. The heat lost through the walls of the combustion chamber to the surrounding air is predominantly by natural convection and radiation and is also affected by atmospheric temperature while that to cooling water is predominantly by forced convection from hot gases to tube wall (function of mass flow of the gases) and conduction.

For the natural gas tests the heat content of the flue gas at the bed temperature is plotted in Figure 4.3 as a function of power input at different excess air levels (O_2% in the flue gas). The figure shows that the flue gas heat content increases with increasing power input. This may be due to higher total mass flow at higher power input for a fixed bed temperature. It can also be seen from the figure that the flue gas heat content increases with increase in O_2 percentage (and hence excess air) in the flue gas despite the corresponding bed temperature decrease. This can be explained on the basis that for a particular total power input the effect of increase in the flue gas mass flow rate outweighs the relatively lower bed temperature.

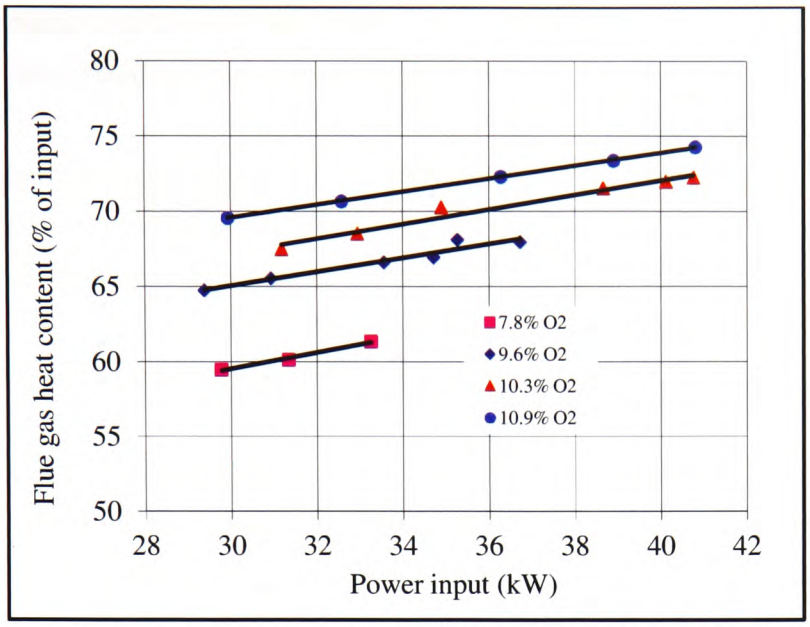


Figure 4.3: Power input vs. flue gas heat content at different excess air levels

Figure 4.4 shows the percentage heat loss to the cooling water, the combustion chamber and the flue gas at bed temperature as a function of power input at 10.3% O_2 in the flue gas. It can be seen from the figure that the percentage flue gas heat loss increases but the percentage rate of loss through the walls of the combustion chamber and cooling water losses decrease with increase in power input. The percentage losses to the cooling water and through the combustion chamber walls are relatively similar with the cooling water being only about 2% greater.

The change in the absolute value of various heat losses can also be estimated fromFigure 4.4e.g. the combustion chamber heat loss at 31 kW thermal input is 15% (4.65 kW) butbecomes below 13% (5.2 kW) at 40 kW. At higher power input, higher air flow rate is required to get the same O_2 concentration in the flue gas i.e. quantity of flue gas increases with increase in power input for same excess air (O_2 % in the flue gas). Thus the velocity of the combustion gases in the plenum chamber increases with increasing power input and this will be associated with an increase in convection to the chamber walls and hence a greater heat loss. The convective heat transfer coefficient is generally proportional to the velocity to the power 0.8 so the heat transfer and hence heat loss does not increase directly in relation to the power input. The wall loss depends upon natural convection and radiation and is a

function of outside wall temperature which would not change much, wall loss is almost constant. So, percentage wall loss decreases as gas flow imcreases.

Figure 4.5 shows the percentage heat loss distribution at different power inputs for 9.6% O_2 in the flue gas. Comparison of Figures 4.4 and 4.5 shows that at higher excess air levels, combustion chamber heat losses are lower than cooling water heat losses (Figure 4.4) and vice versa (Figure 4.5). At higher excess air levels, the flame temperatures in the system are lower thus heat is transferred at a lower rate through the walls of the combustion chamber.

In order to further explain the affect of excess air on the heat loss distribution, the percentage combustion chamber heat losses are plotted against power input at different O_2 concentrations in the flue gas in Figure 4.6. The figure confirms that the combustion chamber heat losses decrease with increase in excess air.

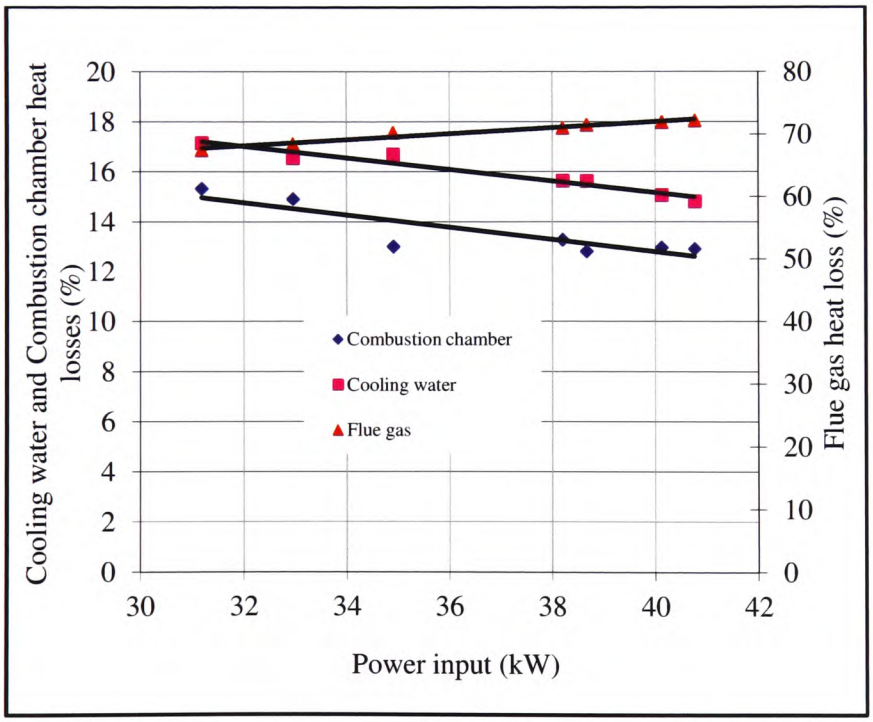


Figure 4.4: Heat loss distribution for natural gas at 10.3% O_2 in flue gas

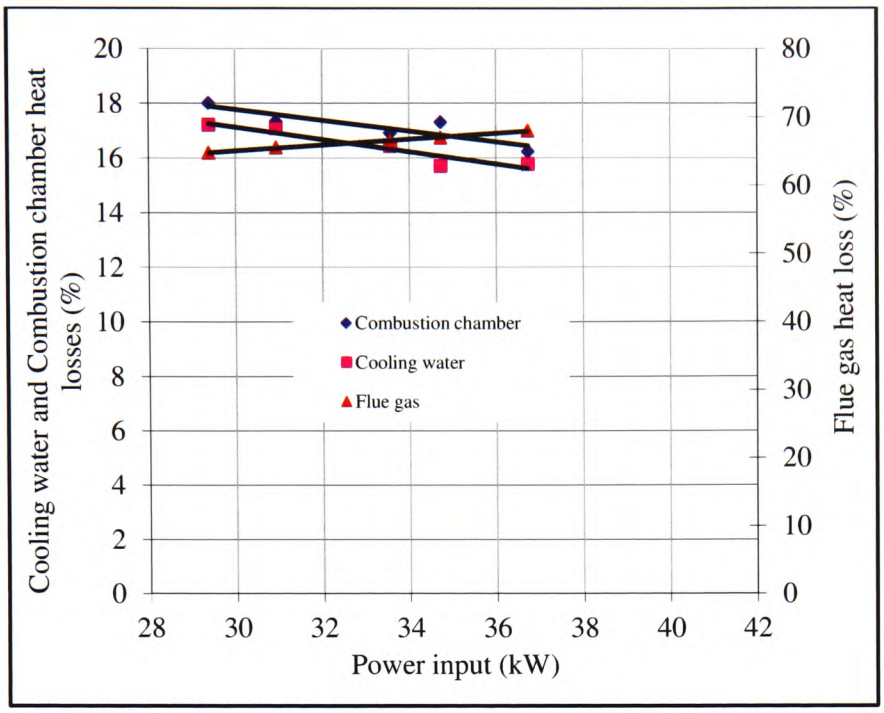


Figure 4.5: Heat loss distribution for natural gas at 9.6% O_2 in flue gas

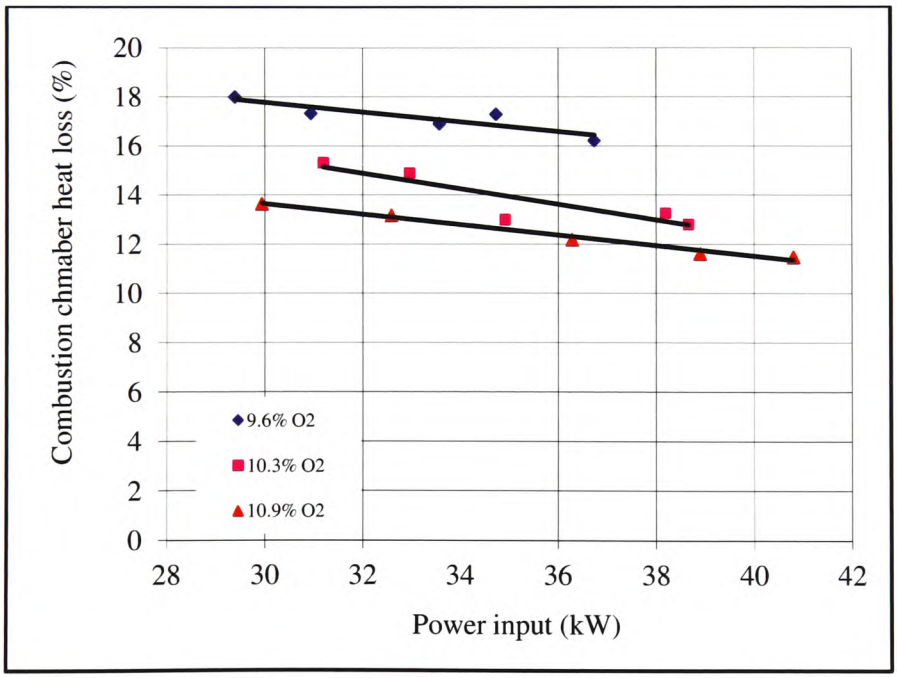


Figure 4.6: Combustion chamber heat losses Vs. power input for natural gas

4.3 Co-firing of natural gas and gas oil:

The experimental programme in this thesis will look at combustion of high moisture biomass so that further initial commissioning tests have been performed with oil and oil-water emulsions. Gas oil and its emulsions were fed to the fluidised bed fired at a fixed temperature with natural gas. Gas oil was fed into the bed to see the response of the bed to its introduction i.e. if its burns in the bed or freeboard and to get more know how about fluidised bed operation when fired with liquid fuels. The emulsions were fired to simulate high moisture biomass e.g. vinasse.

Characteristics of the gas oil used in the tests are given in Table B2, Appendix B, and the procedure of introducing gas oil and emulsion into the bed is explained previously in Chapter 3. The effect of the introduction of the emulsion on the bed temperature was observed while the rig was co-fired with natural gas. Natural gas was fired in the plenum chamber while gas oil was fed into the bed so that only hot flue gases from the natural gas combustion contacted with the gas oil in the bed. In a particular experiment the rig was fired with natural gas at 37 kW input with 11.8% O_2 in the flue gas to get a stable bed temperature of 798 °C. At this point, gas oil was introduced into the bed at a flow rate of 0.9 l/hr, which is equivalent to an energy input of 9.8 kW. Thus combined power input from the natural gas and gas oil was 46.8 kW. It was observed that the bed temperature reached above 930 °C. At this point oil feed was terminated as bed temperature was approaching unsafe limits for fluidised bed combustion conditions due to potential sintering and agglomeration problems at high temperatures.

It is found that the bed temperature with oil feeding can be increased to well above 900 °C, but most of the combustion seemed to be taking place above the bed. This is probably due to the volatile nature of the oil which tends to evaporate quickly when subjected to high temperatures of above 800 °C in the bed. It is also possible that the feeding rate of the oil was high as the combined input from the gas and the oil was around 47 kW which is too high for the size of the bed.

It has also been demonstrated that the stable bed temperature can be achieved with gas oil firing alone. An intermittent flame was observed above the bed indicating that most of the

combustion of the gas oil was taking place above the bed/in the freeboard region. Detailed study of the gas oil combustion in the fluidised bed is beyond the scope of this work. Therefore, further tests were carried out with emulsions of gas oil and water.

4.3.1 Co-Firing of oil water emulsions with natural gas:

Initially in order to gain experience and to investigate co-firing of simulated high moisture biomass combustion in the fluidised bed oil-water emulsions were combusted in the bed at two different emulsion compositions as part of further commissioning tests.

1. 50/50 oil-water emulsion (GCV = 23 MJ/kg, NCV = 20.4 MJ/kg)
2. 30/70 oil-water emulsion (GCV = 13.8 MJ/kg, NCV = 11.2 MJ/kg)

4.3.2 Co-firing Tests with 50/50 emulsion:

The effect of 50/50 oil water emulsion on the bed temperature has been investigated at 5 kW thermal input from the emulsion. The 5 kW input was selected as it was the lowest flow rate available from the feeding pump at the current settings. The emulsion has been tested at different excess air levels and different power inputs (27 – 37.5 kW) from natural gas. The results of the tests are plotted in Figure 4.7 which plots the bed temperature before and after the emulsion introduction as a function of power input from natural gas so that the effect of the additional input from the emulsion (simulated high moisture biomass) can be seen.

The figure shows the bed temperature before and after the emulsion introduction at 9.5% O_2 in the flue gas when rig was fired with natural gas. It can be observed from the figure that the bed temperature increases significantly, in the range of 100 °C, after emulsion introduction although the change in thermal input is only in the range 11.8 to 15.6 % of total power input (5kW from emulsion). The figure also shows that the bed temperature shows a similar trend against power input before and after the emulsion (simulated biomass) introduction. As, can be seen from the figure that bed temperatures after the emulsion introduction are in the range of 880 – 950 °C which particularly at the high power inputs are on the higher side for operation of fluidised beds. Therefore, it was not possible to test the emulsion at higher flow rates (higher power input) due to potential sintering and agglomeration problems at higher

bed temperatures. Although not apparent from Figure 4.7, with the 50/50 oil water emulsion it has been observed that introduction of the emulsion into the bed at bed temperatures below 760 °C results in a drop in the bed temperature instead of raising it. Possible reason could be that most of the combustion of the oil takes place over the bed as described earlier and heat released from this combustion into the bed is not enough to evaporate the water. The energy used to evaporate the water therefore possibly comes from the combustion of natural gas in the bed which results in dropping the bed temperature.

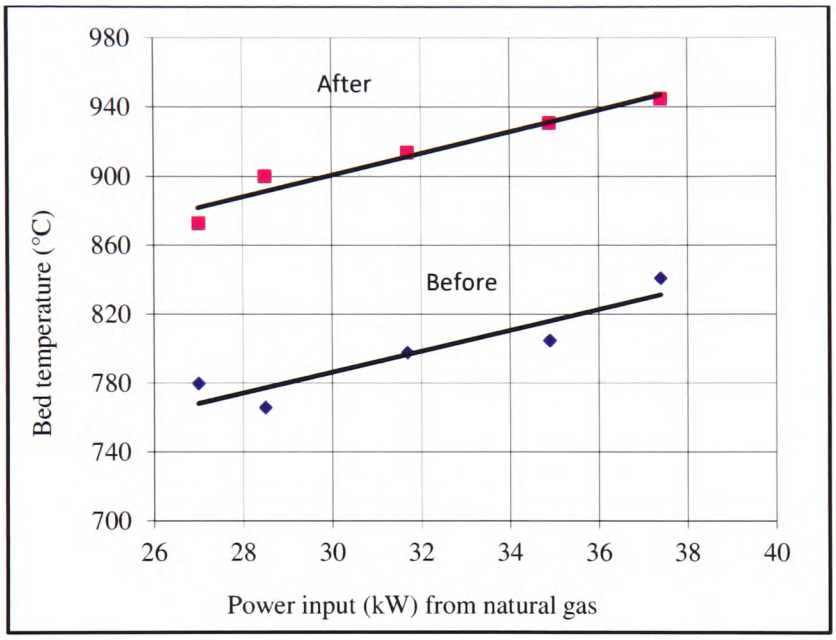


Figure 4.7: Power input vs. bed temperature before and after 50/50 emulsion introduction

4.3.3 Co-Firing Tests with 30/70 emulsion:

To investigate the effect of co-firing with natural gas of a simulated biomass with a higher moisture content experiments have also been performed with 30/70 oil-water emulsion. The results of the experiments are plotted in Figure 4.8 which shows a plot of power input from the emulsion against bed temperature at two different natural gas inputs at 10.3% O_2 in the flue gas (The basis for Figure 4.8 is different from Figure 4.7 because with 50/50 emulsion, only one thermal input setting i.e. the lowest was available while 30/70 emulsion due to its lower CV is tested for three different thermal inputs, for each natural gas input). The 50/50 emulsion has a higher NCV (20.4 MJ/kg) as compared to 30/70 emulsion (11.2 MJ/kg), see

Table 4.2. As can be seen from the figure, the combustion of 30/70 emulsion gives a wider firing range (3 – 14 kW) than the combustion of 50/50 emulsion which was limited to a maximum input of 5 kW due to feeding pump flow limitations. With the 30/70 emulsion a higher power input was possible because of the cooling effect of the higher moisture content. The figure shows that although the introduction of 30/70 oil-water emulsion into the bed raises the bed temperature the rise is considerably lower than that achieved by the 50/50 emulsion. This is because 30/70 emulsion has lower CV and also more energy is required to evaporate relatively higher amount of water which is present in the 30/70 emulsion.

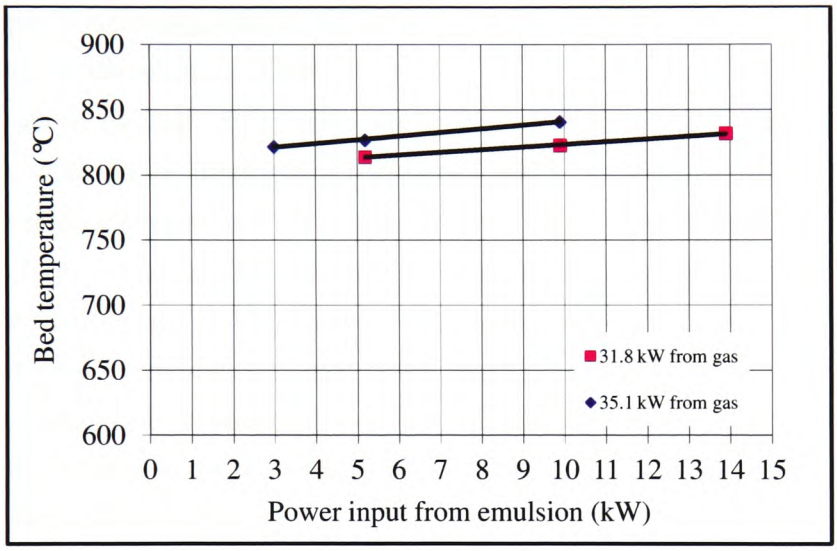


Figure 4.8: Power input vs. Bed Temperature for 30/70 Oil-Water Emulsion

Table 4.2: Calorific values of gas oil and emulsions

	Gas oil	50/50 emulsion	70/30 emulsion
GCV (MJ/kg)	46	23	13.8
NCV (MJ/kg)	43.2	20.4	11.2

Results of the Figure 4.8 are represented in Table 4.3 for clarity. The table shows the amount of natural gas that can be replaced by the introduction of the high moisture content 30/70 emulsion into the bed at specific bed temperatures. [The table shows comparison for three different power inputs from the emulsion (first column) at two different power input from

natural gas at 10.3 % O_2 in the flue gas. Second column shows total power input from the natural gas and the emulsion. Third column shows stable bed temperature at combined power input from the emulsion and natural gas. Fourth column shows the natural gas alone (no emulsion introduction) which is required to get the bed temperature in the third column. Fifth column shows the difference between the combined power input (emulsion + natural gas) and natural gas only requirement to get the same bed temperature (difference of columns 2 and 4)]. It can be clearly seen from the table that the natural gas alone requirement is less than the required combined input from natural gas and emulsion to get the same bed temperature. It can also be seen from the table that the difference between the combined input and the natural gas only input is increasing with an increase in emulsion input. This is probably due to the cooling effect of the moisture in the emulsion and also because the oil in the emulsion is combusted above the bed. For a better understanding of the results, Table 4.4 gives a comparison of the power input from the emulsion which is equivalent to the power input from the natural gas to give a fixed bed temperature. It can be seen from the table that at lower input from natural gas difference between natural gas and equivalent emulsion input is lower e.g. at 31.8 kW and 35.8 kW inputs from natural gas, 5 kW emulsion is equivalent to 4.7 kW and 3.6 kW, respectively, and 10 kW emulsion is equivalent to 6.2 and 5.9 kW, respectively. The higher emulsion thermal inputs again are clearly related to the need to evaporate the moisture in the emulsion as well as possible higher levels of overbed burning because of the volatility of the oil.

4.3.4 Comparison of 50/50 and 30/70 emulsions:

The effect of moisture content of simulated liquid biomass can be seen by comparison of the combustion of 50/50 and 30/70 emulsions on the bed temperature as shown in Table 4.5. The table shows the stable bed temperature corresponding to the addition of 5 kW thermal input from the emulsions for two different natural gas inputs. The corresponding oxygen level in this table is 10.3% in the flue gas. It can be seen from the table that the 50/50 emulsion yields a bed temperature which is 84°C higher at a gas input of 31.8 kW than that with the 30/70 emulsion and 91°C higher at a gas input of 35.1 kW. This reduction in bed temperature with the higher moisture content emulsion is clearly related to the additional heat input which is associated with the evaporation of the additional water in the simulated biomass. Moreover the 50/50 emulsion has a higher calorific value, as mentioned above.

Table 4.3: Comparison of natural gas and 30/70 emulsion results

Emulsion input (kW) Net	Total input (KW)	Bed temperature (°C)	Natural* gas required (kW)	Difference (kW)
35.1 kW from natural gas				
3	38.1	822	37.9	0.2
5	40.1	827	38.7	1.4
10	45.1	841	41	4.1
31.8 kW from natural gas				
5	36.8	814	36.5	0.3
10	41.8	823	38	3.8
14	45.8	832	39.5	6.3

*Data obtained from natural gas only firing at 10.3% O_2 in flue gas

Table 4.4: Natural gas equivalence of the Emulsion

35.1 kW from natural gas			31.8 kW form natural gas		
Emulsion (kW)	Natural gas (kW)	Bed temperature (°C)	Emulsion (kW)	Natural gas (kW)	Bed temperature (°C)
3	2.8	822	5	4.7	814
5	3.6	827	10	6.2	823
10	5.9	841	14	7.7	832

Table 4.5: Bed temperature comparison for 50/50 and 30/70 emulsions

Natural gas input (kW)	31.8	35.1
Bed temperature with natural gas (°C)	785	804
Bed temperature with 30/70 emulsion,5kW (°C)	814	827
Bed temperature with 50/50 emulsion,5kW* (°C)	898	918
Temperature difference[£] (°C)	84	91

*Data taken from a figure similar to one presented in Figure 4.7 but at 10.3% O_2
[£] Difference between the bed temperature with 50/50 and 30/70 emulsion

Calculations show that in the case of 50/50 emulsion, 70 – 95 % of the net energy input of the emulsion is released in the bed; while in the case of 30/70 emulsion it is only 48 – 57% so that this also has an effect. Rest of the energy goes to water evaporation, heat losses, incomplete combustion and freeboard burning.

Section 4.2 has been concerned with some initial experiments on commissioning of the rig with natural gas and provided useful experience on operation of the fluidised bed. However in many ways section 4.3 was more useful since it provided experience on co-firing of different moisture content fuels. Although this was undertaken with natural gas the oil-water emulsions were similar to high moisture content biomass materials so that the experimental data provided useful information on the cooling effect of higher moisture contents on the bed temperatures.

However, most co-firing tests in the thesis will be undertaken with coal so that the next chapter will consider the combustion or co-firing with biomass of this fuel.

Chapter 5

Results and Discussion of the Combustion and Co-Firing Tests with Coal

5.1 Introduction:

This chapter is largely concerned with the results of the bulk of the experimental work in this thesis, i.e. the co-firing tests of biomass, particularly pressed sugar beet pulp with coal. However it initially presents the data for combustion of coal so that the results can be compared with those for co-firing. Variations in bed and freeboard temperatures with changes in thermal input and excess air are discussed. Effect of thermal input and excess air on fluidised bed efficiency (defined later in this chapter) is also discussed.

In the first part of this chapter co-combustion tests of Thoresby coal with wood pellets and wood chips are presented. Effect of moisture content of wood chips during co-firing with coal is discussed and compared with the results of co-firing of low moisture wood chips. Finally, effect of blending ratio of pressed pulp with coal on bed, freeboard temperature and fluidised bed efficiency is discussed. Influence of excess air and thermal input on the temperatures and efficiency is also discussed. The effect of the fuel moisture on the reduction of excess air requirement for a fixed bed temperature is demonstrated.

5.2 Combustion Tests with Thoresby Coal:

Tests were performed with Thoresby singles coal (with a typical size range of 10 to 14mm) at different power inputs and excess air levels. In all the tests a stable bed temperature was achieved. The tests were conducted at net thermal inputs ranging from 8.7 to 18.2 kW at fluidising velocities rangingfrom 1.9 to 3.1 m/s (i.e fluidisation numbers of 3.8 – 6.2) and with the O_2 concentration in the flue gas ranging from 9.7 to 14.5%.

As mentioned previously, during all the tests the rig was fired with natural gas. After achieving a satisfactory bed temperature the rig was switched to solid fuels e.g. coal or biomass and the gas burner was turned off. However, because of the thermal inertia of the insulation inside the plenum chamber, air coming from it remained hot for a period of time. Due to potential variation in bed temperature with the temperature of hot air coming from the combustion (plenum) chamber, stable bed temperature data, plotted in this chapter and elsewhere in this thesis, is taken only at plenum air temperatures of below 100 °C so that the effect of hot air on the bed temperature is a minimum. For example, see Figure 5.1 which plots bed and hot air temperature as function of experimental run time for a particular test. The graph also shows changes in air flow during the test run. The point at which the burner was switched off is also highlighted.

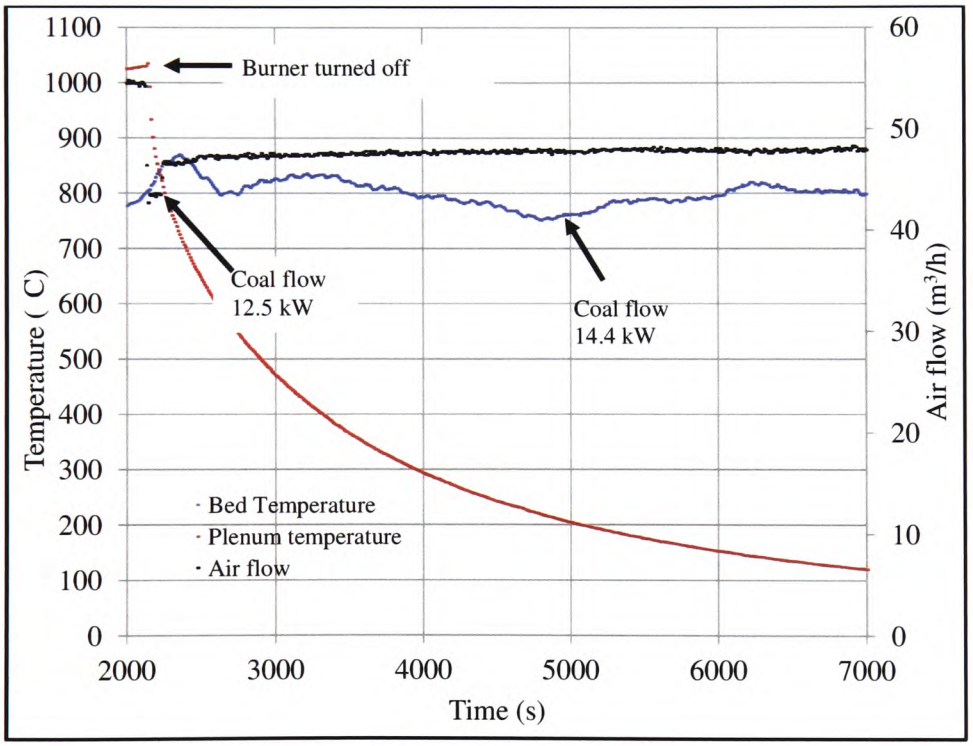


Figure 5.1: Variation in Bed Temperature with change in hot air temperature

Coal feed was started at a thermal input of 12.5 kW and after making sure that the coal started burning, the gas burner was switched off. As can be observed from the figure (5.1) that the plenum temperature sharply came down from above 1000 °C when the burner was switched off but was above 100 °C even 1.6 hours after the gas burner was turned off. The

plot shows that air flow was kept constant at about 48 m^3/h after a reduction when the rig was switched from natural gas to coal as with coal firing lower input can give desired temperatures and thus required lower air flow rate. As can be observed from the figure that the bed temperature is strongly influenced by the plenum chamber and came down to as low as 750 °C when the plenum temperature reduced to 200 °C at which point coal flow had to be increased to an equivalent of 14.4 kW to stop the temperature getting too low to be sustainable. As can be observed from the plot, that bed temperature almost stabilised at 800 °C when the plenum chamber temperature approached 120 °C. Therefore, in order to ensure that the influence of the plenum chamber temperature on the stable bed temperature is minimal, the data is only taken at plenum temperatures below 100 °C.

It was observed during the tests that the bed and the freeboard temperatures were dependent upon the excess air levels or oxygen content of the flue gas. Some temperature variation occurred with changes in thermal input at a particular oxygen level and probably resulted from the consequent substantial changes in fluidising velocity. However, generally these variations were less significant than the typical variations in the bed and freeboard temperatures with changes in the flue gas oxygen content and hence excess air level which are presented in Figure 5.2 for a net thermal input of 18.2 kW.

The figure shows that at lower O_2 concentrations the freeboard temperature (FBT_1) at 0.24m above the bed is lower than the bed temperature. A possible explanation is that the flue gas loses heat as it passes up through the containment tube. Thus, the temperature of the flue gas drops along the tube height. However as the O_2 concentration in the flue gas increases the freeboard temperature (FBT_1) and the bed temperature approach each other and at a certain higher O_2 concentration the freeboard temperature (FBT_1) becomes even higher than the corresponding bed temperature.

This can be explained on the basis that as the excess air level is increased at a constant thermal input, and hence coal feed rate, the fluidising velocity is increased due to increased flow rate of the flue gas. Therefore the close agreement between the bed and freeboard temperature (measured at a height 0.24m above the static bed) at high oxygen levels may be partially due to the fluidised bed expanding up to this location as a result of higher fluidising velocities. However this effect was not observed when firing with natural gas at even higher

fluidising velocities so that a more likely explanation is the heat release from the combustion of the volatiles above the bed. This heat release more than compensates for the approximate heat loss from the walls of the containment tube of 1.5 kW over this height so that the freeboard temperature is increased relative to the bed temperature.

Figure 5.2 shows that the freeboard temperature FBT_2 is considerably lower than the bed temperature as well as freeboard temperature FBT_1 due to heat loss through the walls of the containment tube. The FBT_1 and FBT_2 temperature profiles are almost parallel which suggests that there is a linear relationship between the heat loss through the wall of the containment tube and the freeboard temperatures. The parallel relationship between FBT_1 and FBT_2 also explains that heat lost through the walls of the containment tube between these two locations is constant and is independent of oxygen concentration of the flue gas i.e. flue gas flow rate.

Figure 5.3 shows a graph similar to Figure 5.2 but for a lower thermal input of 10.6 kW. Both of the figures show a similar trend of decline in bed and freeboard temperatures with increase in excess air levels. Also, Figure 5.3 shows a similar trend to that of Figure 5.2 in that freeboard temperatures FBT_1 and FBT_2 are lower than the bed temperature and that FBT_1 and FBT_2 are almost parallel. Both of the Figures, 5.2 and 5.3, show that freeboard temperature FBT_1 approaches bed temperatures as excess air level is increased due to increased over bed burning and at a certain higher excess air level both temperatures profiles BT and FBT_1 cross each other i.e FBT_1 becomes higher than BT. The condition is reached at about 13.3% O_2 in flue gas in the case of 18.2 kW thermal input but at lower input of 10.6 kW the condition is seems to be achieved at above 14% O_2 in the flue gas. Thus, at lower thermal inputs overbed burning is lower as compared to higher thermal inputs due to lower overall air flow at a specific excess air level and thus lower fluidising velocity. Therefore, lower thermal inputs result in more fuel being burned in the bed and less in the freeboard.

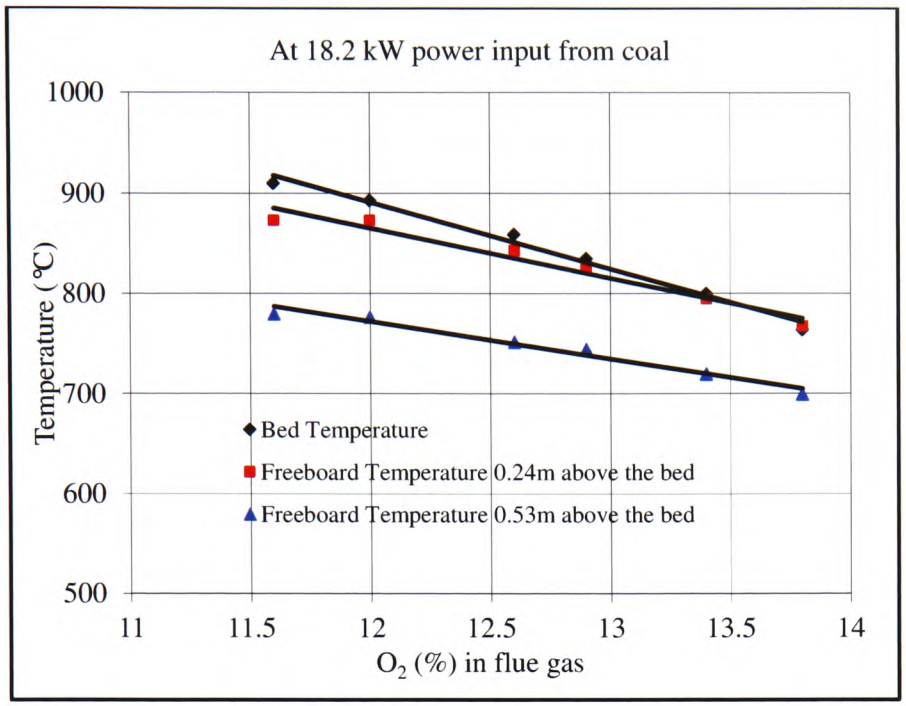


Figure 5.2: Bed and Freeboard Temperatures with Thoresby coal at 18.2 kW

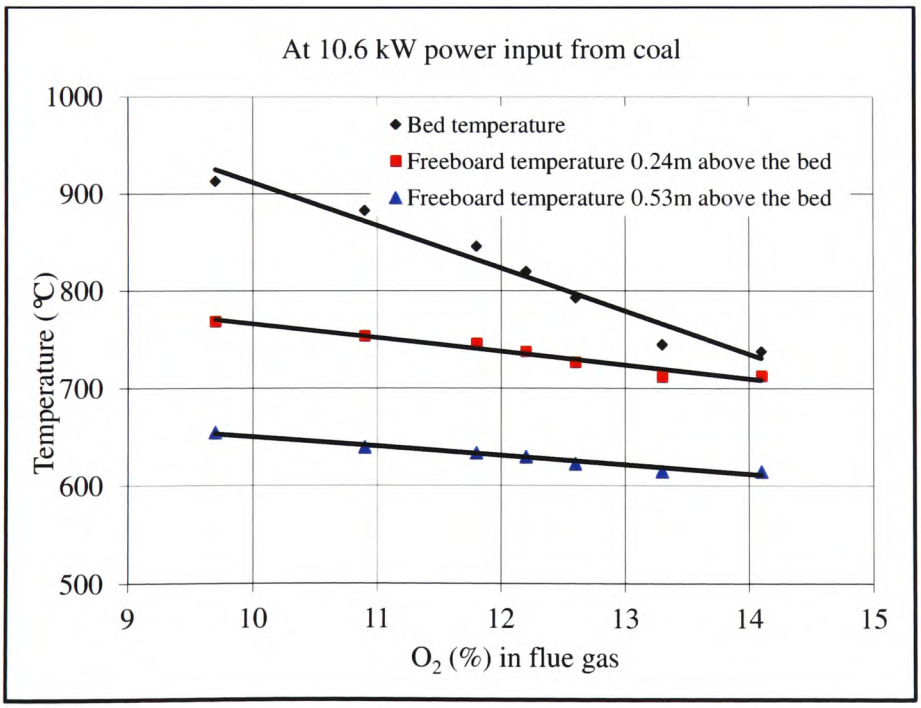


Figure 5.3: Bed and Freeboard Temperatures with Thoresby coal at 10.6 kW

The comparison of the two figures shows that at lower thermal inputs lower excess air is required to achieve a specific bed temperature. For example, to achieve a bed temperature of 850 °C, 11.4% O_2 in flue gas is required at 10.6 kW thermal input while to achieve the same bed temperature at 18.2 kW, 12.6% O_2 (an increase of more than 10%) in flue gas is required. The difference between O_2 levels to achieve a set bed temperature at different thermal inputs decreases with increase in O_2 levels and with decrease in bed temperatures, see Figure 5.4 which compares bed temperatures as function of O_2 in flue gas for the two thermal inputs. The Figure shows that to achieve a bed temperature of 800 °C, 12.5% O_2 in flue gas is required at 10.6 kW thermal input while to achieve the same bed temperature at 18.2 kW, 13.4% O_2 (an increase of around 7%) in flue gas is required. The figure shows that the gap between the two temperature profiles is becoming narrower as the temperature is decreased or as the O_2 level in the flue gas is increased. The reason may be that the overbed burning of volatiles and fine char increases with an increase in excess air and thus fluidising velocity. The effect of the overbed burning is higher at higher thermal inputs than at lower ones because at higher thermal inputs total mass of air and thus fluidising gases is comparatively higher. Also at higher thermal inputs total volatile charge is higher which tends to burn above the bed at higher fluidising velocities.

The comparison of the figures 5.2 and 5.3 also shows that the freeboard temperatures, relative to bed temperatures, are considerably lower at lower thermal input of 10.6 kW as compared to those at 18.2 kW. For example, see Figure 5.5 which plots freeboard temperatures against O_2 in the flue gas for the two thermal inputs. The figure shows that freeboard temperature corresponding to a bed temperature of 910 °C at 18.2 kW thermal input is 873 °C, while for a similar bed temperature of 913 °C at 10.6 kW thermal input corresponding freeboard temperature is only 769 °C, which is more than 100 °C lower. This can again be explained on the basis of the above argument that at lower thermal inputs, because of lower air flow, overbed burning is reduced and more of the fuel burns in the bed. The figure also shows that the gap between the two temperature profiles becomes narrower at higher O_2 (excess air) levels in the flue gas. This again may be due to increase in overbed burning at higher air flow rates and thus fluidising velocities.

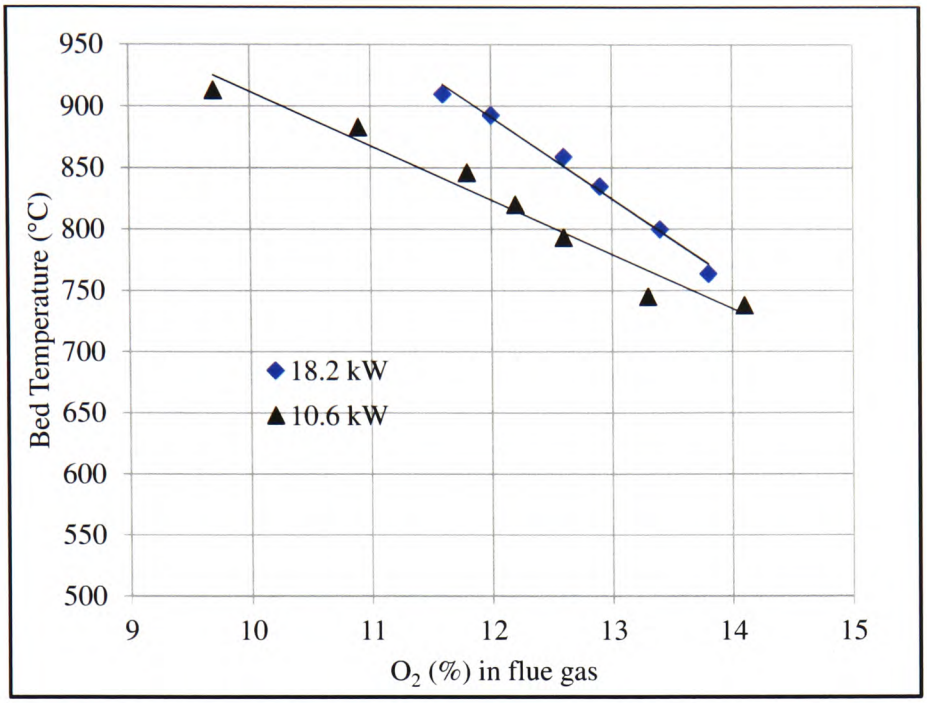


Figure 5.4: Comparison of bed temperatures for different coal thermal inputs

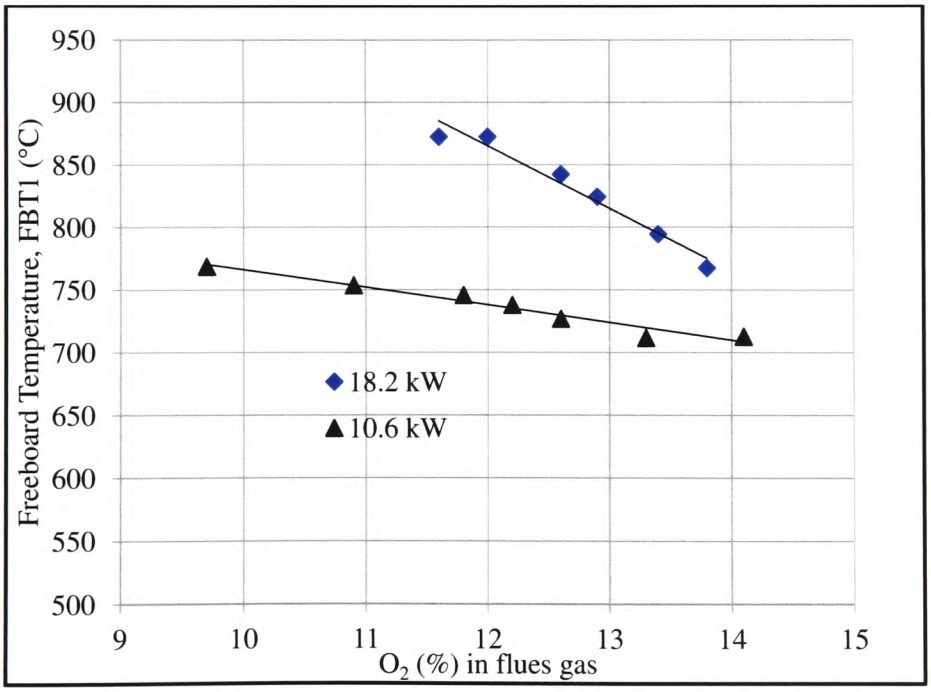


Figure 5.5: Comparison of freeboard temperatures for different coal thermal inputs

The purpose of the fullscale fluidised bed at British Sugar is to produce, as efficiently as possible, hot combustion products which are subsequently used to dry pressed sugar beet pulp in a large rotary drier. Consequently a so-called "fluidised bed efficiency" was defined based on either the bed or freeboard temperature by calculating the enthalpy of the combustion products at these temperatures. This enthalpy can then be expressed as a percentage of the total thermal input (i.e. the chemical energy in the fuel together with the sensible heat content in the fluidising air) less the heat loss to the water cooled distributor and the appropriate casing loss i.e. the energy available in the rig after losses are taken into account. It is therefore a measure of the efficiency with which hot combustion products are generated by combustion in the test rig. Method of calculation of the efficiency is given Appendix C. As would be expected, because of the overbed burning of some of the volatiles, the fluidised bed efficiencies based on the freeboard temperatures are higher than those based on the bed temperatures, see Figure 5.6 which plots fluidised bed efficiency against O_2% at bed temperature and freeboard temperature (FBT_1). The difference in efficiencies between the two positions increases as the oxygen concentration and hence the fluidising velocity and excess air level increases. For example, at 10.6% O_2 in flue gas efficiency at BT is around 77% while that at FBT_1 is around 81%, an increase of around 5%. However, at higher excess air level of 13.8% O_2 in flue gas efficiency at BT is around 82% while that at FBT_1 is around 90%, an increase of around 10%. This indicates that more heat is released above the bed at higher oxygen levels possibly due to higher fluidising velocities and better mixing as a result of higher flow rate of the flue gas at higher excess air levels. Overall, efficiency improved from 77 to 81% at BT, an increase of 6.5% and from 82 to 90% at FBT_1, an increase of 11%, over the 10.6 to 13.8% O_2 level variation in flue gas. Fluidising velocity for this excess air range varies from around 2.1 to 2.4 m/s, see Figure 5.6, which is an increase of almost 14%. The results are in agreement with the variations in the temperature profiles observed in Figures 5.2 and 5.3.

Figure 5.7 shows a similar plot of fluidised bed efficiency against O_2 concentration in the flue gas at a lower thermal input of 10.6 kW. Again the plot shows similar trends as are observed in Figure 5.6 that the efficiencies at FBT_1 are higher than those at BT due to overbed burning of volatiles and possibly fines and that the difference between the two efficiencies increases with increase in excess air (O_2 concentration in flue gas). For example, at 9.7% O_2 in flue gas, efficiency at BT is around 68% while that at FBT_1 is around 73%, an increase of around

7%. However, at higher excess air level of 14.1% O_2 in flue gas efficiency at BT is around 84% while that at FBT_1 is around 96%, an increase of around 14%. Overall, efficiency improved from 68 to 84% at BT, an increase of 23% and from 73 to 96% at FBT_1, an increase of 31%, over the 9.7 to 14.1% O_2 level variation in flue gas. The fluidising velocity for this excess air range varies from 1.05 to 1.42 m/s which is very much lower than the fluidising velocities calculated at 18.2 kW thermal input from coal.

Comparison of the data shows that the rate of change of efficiency at both of the temperatures, BT and FBT_1, is higher at lower thermal input of 10.6 kW as compared to higher thermal input of 18.2 kW. At lower excess air levels the efficiencies at BT and FBT_1 are lower for lower thermal input while at higher excess air levels it is vice versa. For example at 11.6% O_2, efficiency at BT for 10.6 kW input is around 74% while that for 18.2 kW is around 77%. Similarly the efficiency at FBT_1 for 10.6 kW input is around 80% while that for 18.2 kW is around 82%, see Figure 5.8, which shows efficiencies at BT and FBT_1 for 10.6kW and 18.2 kW thermal inputs on the same graph. It can be clearly observed from the plot that the efficiency profiles for 10.6 kW are steeper as compared to those at 18.2 kW. It may be due to lower air flow (fluidising velocities), at a specific excess air level, at lower thermal inputs. As the excess air level (air flow) is increased turbulence increases and air fuel mixing improves and results in better combustion. The influence of increment in excess air levels on efficiencies is more pronounced at lower thermal inputs which may be due to lower amount of total mass in the bed which is influenced comparatively at a higher rate with changes in fluidising velocities.

Similar trends were observed at other thermal inputs and overall during the tests the "fluidised bed efficiency" varied from around 68 to 85% based on the bed temperatures (BT) and 75 to 98% based on the freeboard temperatures (FBT_1) measured at a height of 0.24m above the static bed.

The above results show that overall the tests with Thoresby coal yielded self consistent data for the performance of the pilot scale fluidised bed and provides a sound basis for comparison when firing various coal-biomass blends.

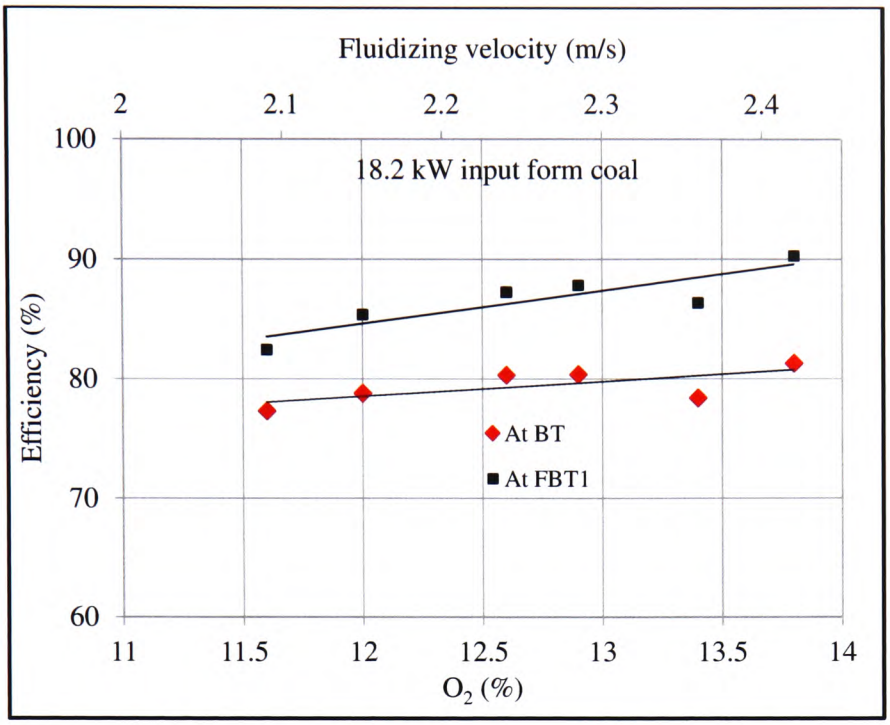


Figure 5.6: Fluidised Bed Efficiencies at 18.2 kW coal input

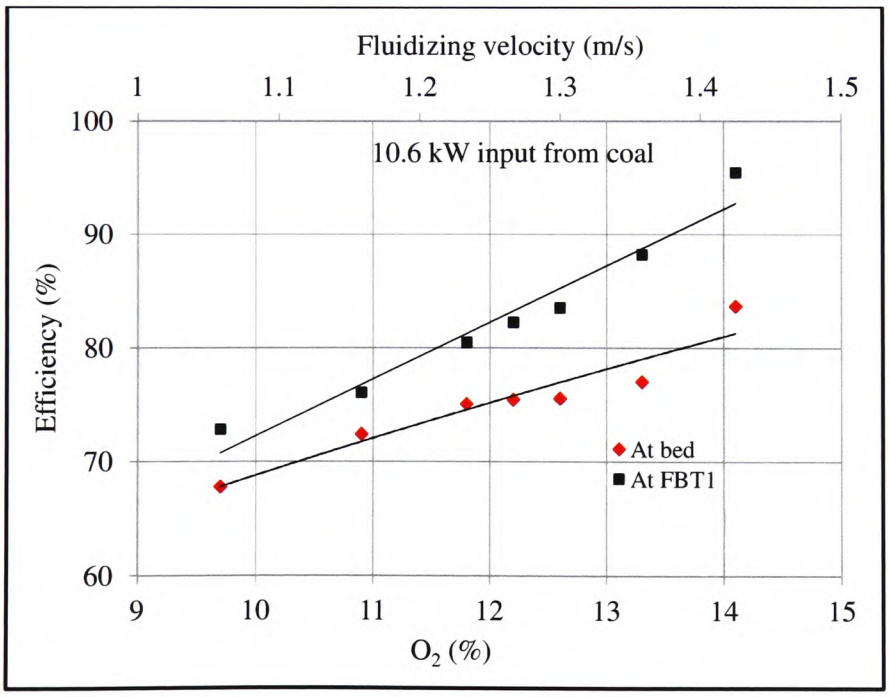


Figure 5.7: Fluidised Bed Efficiencies at 10.6 kW coal input

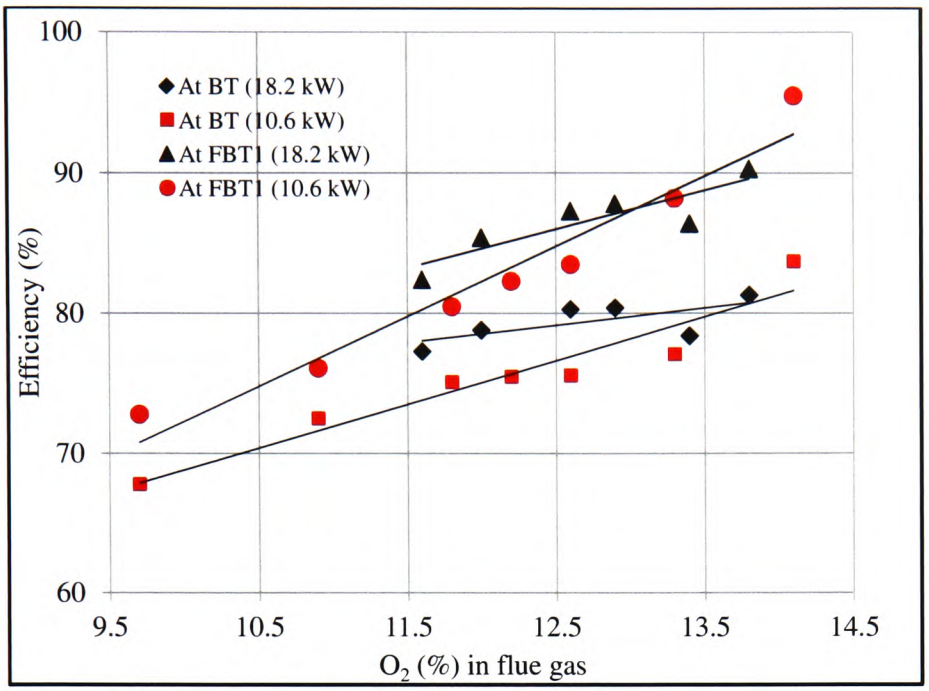


Figure 5.8: Comparison of efficiencies at different thermal inputs

5.3 Co-Firing of Wood Pellets with Coal:

After getting baseline data with Thoresby coal initial co-firing tests were undertaken with wood pellets, a prepared biomass fuel with low ash and moisture content and with a relatively consistent size and composition. The fuel is easy to burn so that prior to co-firing, tests were undertaken when burning the pellets alone. Results of the tests are summarised in Table 5.1. Typical variations in the bed and freeboard temperatures with the oxygen level in the combustion gases, at 10.2 kW thermal input, are presented in Figure 5.9. Comparison of these results with the data in Figure 5.3 indicates that the pellets can be burnt with a lower excess air level (i.e. with a lower oxygen concentration in the flue gases) to get the same bed temperatures as compared to coal. For example at a bed temperature of 850 °C the oxygen level when burning coal was 11.5% whereas it was only 10% when burning pellets, see Figure 5.10, which shows comparison of bed and freeboard temperatures at almost same thermal input for coal (10.6 kW) and wood pellets (10.2 kW). This is due to lower stoichiometric air requirement for pellets (5.4 kg/kg) as compared to that for coal (9.6 kg/kg) because pellets have lower carbon (just above half) and higher oxygen content (almost 5.5 times) as compared to Thoresby coal.

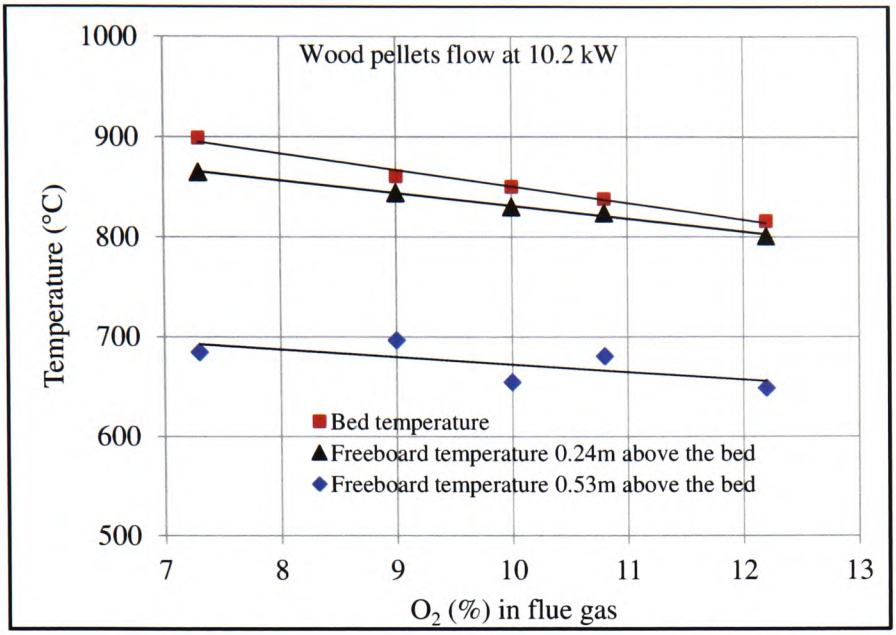


Figure 5.9: Bed and freeboard temperatures with wood pellets

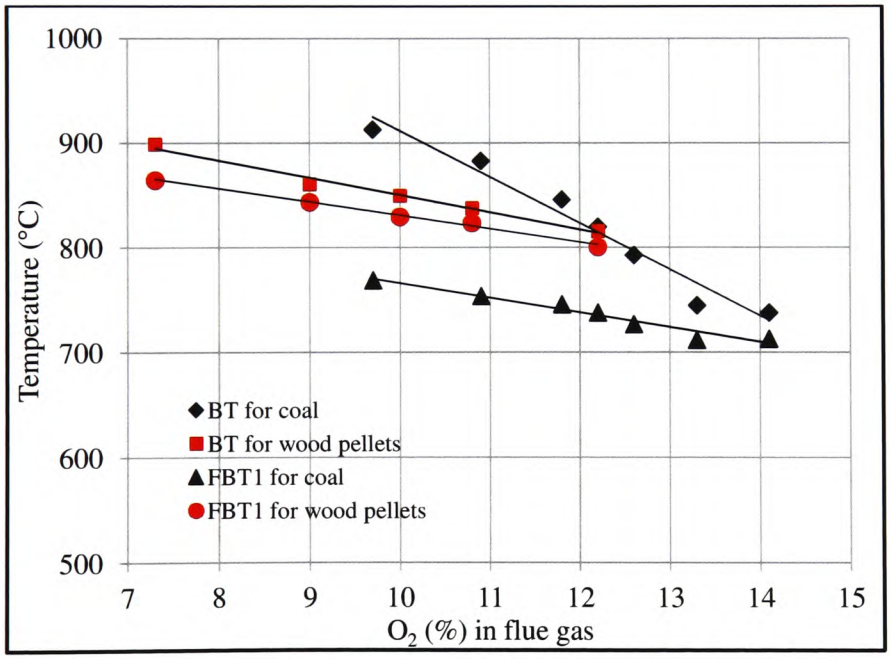


Figure 5.10: Comparison of BT and FBT_1 for coal (10.6 kW) and wood pellets (10.2 kW)

Table 5.1: Results of Pellets and 50/50 Coal-Pellets Blend Co-Firing

	Pellets	50/50 coal-pellets blend
Power input (kW)	7.9 – 12.5	9.6 – 12.2
O_2 (%) in flue gas	7.3 – 13.7	10.2 – 14
Efficiecny at BT (°C)	68 – 96	68 – 83
Efficiency at FBT_1 (°C)	81 – 100	76 – 95
Fluidising velocity (m/s)	1.3 – 2.2	1 – 1.7

As would be expected a blended fuel with a 50/50 mix by mass of pellets and coal exhibited an intermediate behaviour when compared with the individual single fuels, see Figure 5.11 which presents the bed and freeboard temperatures for 50/50 coal and pellets blend. In this case a bed temperature of 850°C is achieved at an oxygen level of about 11.3% as compared to 11.5% and 10% in the case of coal and pellets only combustion, respectively. A likely explanation is that stoichiometric air to fuel ratio for the blend is 7.5 (kg/kg) which is in-between that for coal and pellets.

Composition of 50/50 coal-pellets blend on as received, dry and dry ash free basis is given Table 5.2. The higher net calorific value of the coal results in this fuel contributing about 64% of the net thermal input despite the mass flow rates of the two components being the same, see Table 5.3 which gives mass and calorific value contribution of coal and pellets in the blend. This is possibly the reason that the results with 50/50 blend are inclined towards coal e.g. expected O_2 levels at 850 °C bed temperature for 50/50 blend on the basis of the results obtained for individual fuels is 10.75% but actually measured value is 11.3% which is possibly due to the higher contribution of coal towards net calorific value of the blend. Also although dry mass contribution of both of the fuels is almost the same (49.1/50.9), stoichiometric air requirement for coal is 9.6 (kg air/kg fuel) is almost 1.8 times higher than that for pellets, 5.4 (kg air/kg fuel). This results in lower bed temperature and higher O_2 levels in the flue gas for pellets than for coal at a fixed air and fuel flows. The 50/50 coal and pellets blend shows an intermediate behaviour.

As explained above that comparison of the results show that the temperature profiles are dependent on the mass fraction of different fuels in the blend. Similar results were obtained

by Kuprianov *et al* (2006) who found by co-firing rice husk and sugar cane bagasse in a conical fluidised bed combustor that temperatures in the combustor were independent of excess air but were dependent on the energy fraction of rice husk which was weakened as the energy fraction was increased. However, during present study it is observed that BT and FBT are dependent upon excess air and decrease with increase in the amount of excess air.

Table 5.2: Analysis of 50/50 Coal-Pellets Blend

50/50 Coal-Pellets blend analysis			
	As received Basis	Dry basis	DAF basis
Moisture (%)	7.15	-	-
Ash (%)	2.7	2.9	-
Carbon (%)	60.11	64.67	66.6
Hydrogen (%)	4.78	5.14	5.3
Oxygen (%)	23.19	24.94	25.69
Nitrogen (%)	0.85	0.91	0.94
Sulphur (%)	1.01	1.09	1.12
Chlorine (%)	0.32	0.34	0.35
St. A/F ratio	7.5 kg/kg		
Net CV (MJ/kg)	23.4		

Table 5.3: Mass and calorific value contribution of coal and pellets in 50/50 blend

	Energy content (MJ/kg)	Dry mass
Coal contribution (%)	64.2	50.9
Pellets contribution (%)	35.8	49.1

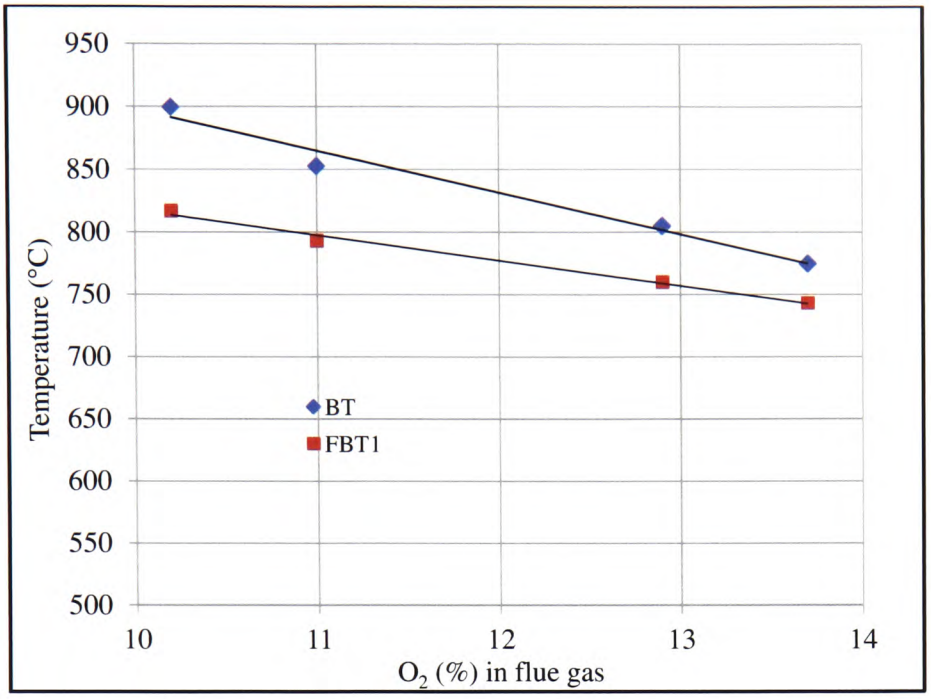


Figure 5.11: Bed and freeboard temperatures with 50/50 Blend of coal and pellets

A comparison of Figures 5.9 and 5.11 shows that the difference between the bed and the freeboard temperature is higher in the case of co-firing (Figure 5.11) as compared to biomass only firing (Figure 5.9) i.e. the freeboard temperature is closer to the bed temperature in the case of biomass only firing as compared to co-firing. This can again be explained on the basis of the phenomenon of overbed burning of the volatiles which is higher in the case of biomass only firing due to higher volatile content of wood pellets. As an example at 11% O_2, the bed and the freeboard temperatures in the case of co-firing are 850 °C and 795 °C, respectively while in the case of biomass only firing the bed and freeboard temperatures at 11% O_2 are 830 °C and 820 °C, respectively, see Figures 5.12 and 5.13, which shows comparison of bed and freeboard temperatures for different fuels, respectively.

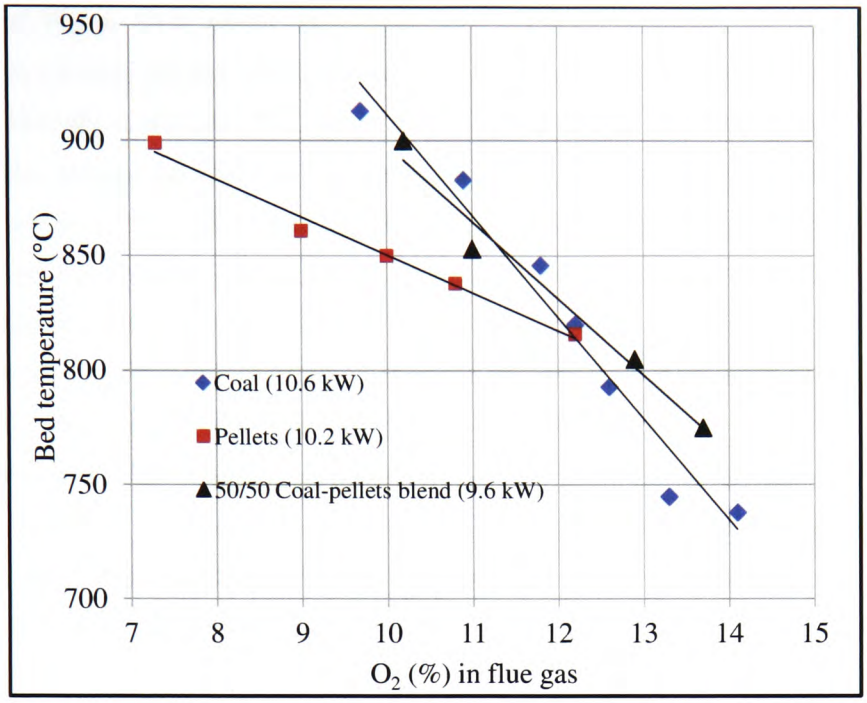


Figure 5.12: Comparison of Bed temperature for different fuels

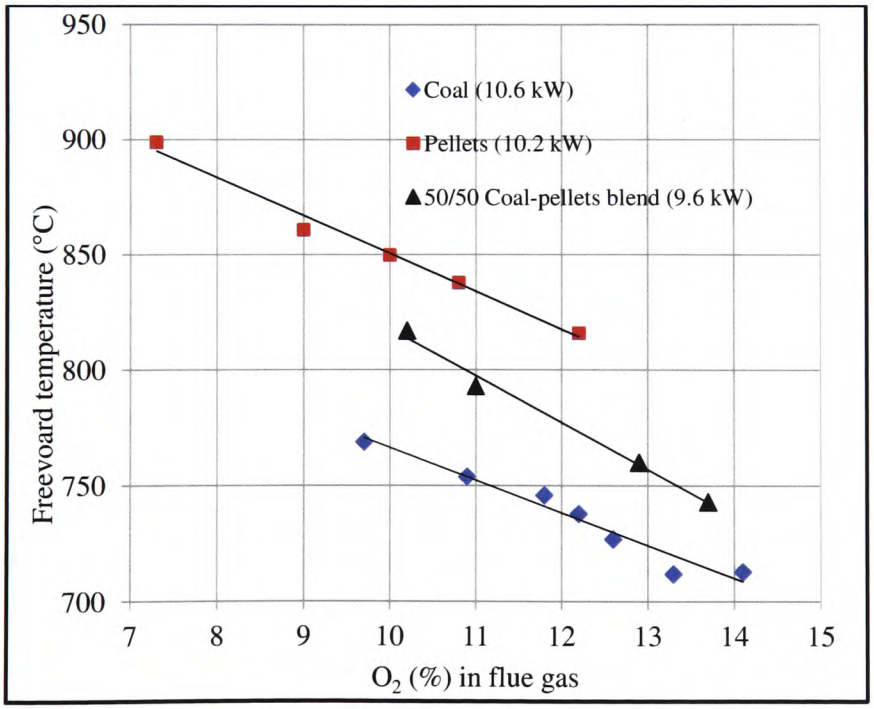


Figure 5.13: Comparison of freeboard temperature for different fuels

Analysis of Figure 5.12, which shows plots of O_2 concentration in flue gas against bed temperature for coal, pellets and their 50/50 blend (by mass) reveal that all the three fuels behave differently in the bed. The slopes of the three temperature profiles are different. The profile is the steepest for coal followed by co-firing and then pellets. This indicates that the influence of excess air is the highest for coal firing followed by blend and then pellets alone. This may be due to different reactivities of biomass and coal. Biomass is generally more reactive than coal. At lower excess air levels and thus O_2 concentrations, bed temperature is higher and coal is consumed relatively quickly. As the excess air level increasees temperature drops and combustion rate of coal also decreases which results in sharper drop in bed temperature. Also, due to higher fluidising velocity at higher excess air levels, elutriation of fine char may have increased which could have resulted in lower bed temperatures. In the case of biomass, due to higher reactivity, excess air level and temperature have not that much influence on rate of combustion and because of lower fixed carbon chances of char elutriation for biomass are also lower. That is why the temperature profile for pellets is flatter as compared to that for coal.

The figure shows that behaviour of coal-pellets blend is very much different to that of coal. For lower excess air levels bed temperature for the blend is lower than that for coal. As the excess air is increased, both profiles cross each other (at around 11.4% O_2) and bed temperature for the blend becomes higher than that for coal. The reason could be that for the same thermal input total mass of the blend is higher as compared to coal due to lower CV of pellets. At lower excess air levels, it is possible that there is not enough oxygen available for combustion or mixing is not adequate and availability of oxygen to coal is restricted by pellets around it. At higher excess air levels, combustion rate increases due to enhanced mixing and oxygen availability and thus bed temperature increases.

Figure 5.13, which presents comparison of freeboard temperatures as a function of O_2 in the flue gas for the three fuels e.g. coal, pellets and their 50/50 blend shows that the freeboard temperature in the case of biomass only firing is the highest followed by co-firing and coal only firing. This explains the increased overbed burning with increase in biomass proportion during co-firing due to higher volatile content of biomass. The comparison of bed and freeboard temperatures also shows that at a fixed excess air level freeboard temperature in the case of biomass only firing is higher than co-firing although power input in the case of co-

firing (9.6 kW) is lower than the biomass only firing (10.2 kW) case while the bed temperature in the case of biomass only firing is lower than in the case of co-firing, an obvious effect of overbed burning.

For clarity, the results of bed and freeboard temperatures for coal, pellets and their blend at 11% O_2 in the flue gas are presented in Table 5.4. The table shows that the difference between the bed and the freeboard temperature is the highest in the case of coal only firing followed by co-combustion and biomass due to the increased volatile burning in the freeboard region in the case of increased biomass input. The observed phenomenon of freeboard temperature being higher in the case of higher biomass input was also demonstrated by Changquing *et al.* (2002) who co-fired MSW and coal in a 0.2 MW_{th} CFB and found that the temperature in the freeboard region was 100 – 300 °C higher than that with coal only firing due to combustion of volatiles in this overbedregion. Similar behaviour was observed by Cliffe and Patumsawad (2001) who stated that fuels having higher content of volatiles tend to burn above the bed and therefore do not always provide enough heat to maintain the temperature of the bed. They found that freeboard temperature with 10% olive oil waste in coal was higher than 100% coal even though bed temperature was lower due to significant burning of olive oil waste in the freeboard.

Table 5.4: Comparison of Bed and Freeboard temperatures for Coal, Biomass and their blend

	At 11% O_2 in the flue gas		
	Coal (10.6 kW)	Coal-pellets, 50/50 blend (10.2 kW)	Wood pellets (9.6 kW)
Bed temperature (°C) BT	875	850	830
Freeboard temperature (°C) FBT_1	750	795	820
Difference (°C) BT-FBT_1	125	55	10

The fluidised bed efficiencies with pellets varied from about 75 to 96% based on bed temperature and 82% to virtually 100% based on the freeboard temperature depending upon the excess air level. As an example, the efficiency data is plotted against O_2 (%) for a particular thermal input of 10.2 kW in Figure 5.14. The figure shows that the efficiency at BT is consistently higher (by around 10%) than that at FBT_1. This again indicates that the

combustion of some of the volatiles occurs in the overbed region. The fluidised bed efficiency with 50/50 coal-pellets blend ranges from 65 to 80% based on BT and 73 to 91% based on FBT_1. The data shows that efficiency for 50/50 coal-pellets blend is lower than pellets possibly due to elutriation of coal char.

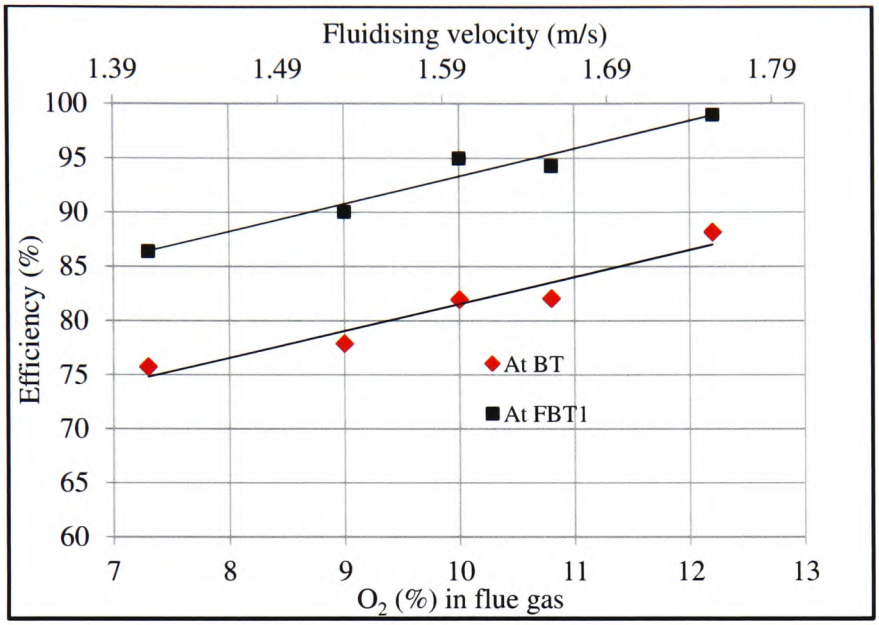


Figure 5.14: Efficiencies at BT and FBT_1 for pellets

In order to better understand the behaviour of the coal and other fuels during combustion in a fluidised bed it is important to know the different processes occurring in and above the bed, see Figure 5.15. When a cold particle of fuel enters a hot fluidised bed of inert solids (at 800 – 900 °C), it is heated up by collision with the hot bed particles. The heat transfer coefficient from the bed particles to the coal particles with diameters between 5 – 10 mm is around 300 W/m^2K. Thus at a temperature difference of 800 °C, the heat flux at the surface of the particle is 240 kW/m^2[Basu, 2006] so that the fuel particle is heated up at a rate of around 100 °C/s. The de-volatilisation step lasts for 10 – 100 s depending upon the coal type and char burning takes around 100 to 2000 s. Typicalresidence time of volatiles in fluidised beds is several seconds and hence they may leave the bed without contacting oxygen so it is necessary that they burn in the freeboard. On the other hand char stays in the bed for a long time and certainly will see oxygen rich zones during its combustion history [Oka and Anthony, 2003]. Biomass has higher volatile matter and lower char content than coal. Thus higher coal input

means higher char input which continues to burn in the bed for a longer time resulting in higher bed temperatures as compared to biomass, as discussed earlier.

The volatiles content of coal (percentage of combustibles) is typically 38.2% whereas that of the pellets is 81.94% which is more than twice that of coal, see Table 5.5. On the other hand the fixed carbon content for coal is 61.8% whereas that of pellets is 18.06% which is more than three times lower than coal. A 50/50 blend of coal and pellets has a volatile content of 60.23% and fixed carbon content of 39.77%. Volatiles to fixed carbon ratio for pellets is more than 7 times that for coal. For 50/50 coal-pellets blend the ratio is around 2.5 times that for coal. Thus with coal combustion bed temperature is expected to be higher than that in the case of pellets due to higher char input and freeboard temperature in the case of pellets combustion is expected to be higher due to higher volatiles content of pellets. A 50/50 blend of coal and pellets is expected to show intermediate behaviour as observed during the tests and explained in the above paragraphs.

The results are in line with the findings of Sjaak and Jaap (2008) who stated that the type of fuel influences the combustion process by various characteristics such as fuel composition. Volatile content and thus reactivity of different biomass fuels is different and influences the thermal behaviour of the fuel and this behaviour is also influenced by the structure and bond present in biomass fuels. This results in very different de-volatilisation behaviour as a function of temperature.

According to theASTM classification Thoresby coal falls in a high volatile category (> 31% volatile matter) [ASTM, 2004]. Ignition of high volatile coals is a two stage phenomena, the combustion of volatile matter and the combustion of fixed carbon [Sami *et al* 2001]. Volatiles evolved from the fuel continue to burn as the gases move up in the freeboard if there is not enough time for the volatiles to burn in the bed under the operating conditions. With increase in O_2 concentration, mass flow of the flue gas increases at a fixed thermal input. This results in increased fluidising velocities which increase the dispersion of the volatiles so that a higher proportion burns in the freeboard. Also at high fluidising velocities mixing of the fuel and bed material improves and hence strong combustion zones move up [Armesto *et al* 2002].

Table 5.5: Volatiles and Fixed carbon (Percentage of combustibles) of fuels tested

	Volatiles (%)	Fixed carbon (%)	V/FC	Normalised V/FC with coal
Coal	38.2	61.8	0.62	1
Pellets	81.94	18.06	4.54	7.32
50/50 Coal-pellets	60.23	39.77	1.51	2.44

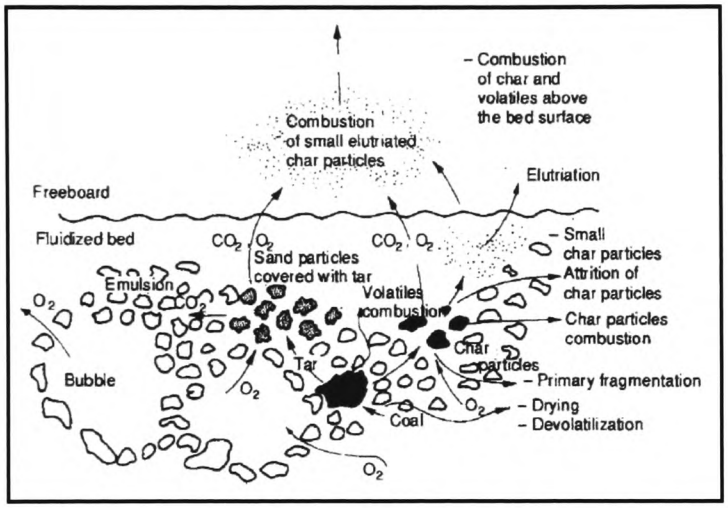


Figure 5.15: Different processes during Fluidised Bed Combustion of Coal [Oka and Anthony, 2003]

Concentration of O_2 in the bed is heterogeneous due to the hindrance offered by inert bed particles to the mass transfer of O_2 towards fuel particles. So, it is also possible that the volatiles may leave the bed without contacting oxygen and continue to burn largely in the freeboard.

Moreover, as the fuel is fed over the bed during the tests, the properties of the fuel particles reaching the bed are not the same as those entering the furnace as described by Oka and Anthony (2003). The fuel particles can partially or totally lose their moisture, and depending upon the size of the particles, fuel characteristics, freeboard temperature and time the particle takes to reach the bed surface the release of volatiles and burning of char can start even

before the particles reach the bed surface. All these factors can contribute to the higher freeboard temperatures than expected which are sometimes even higher than the corresponding bed temperature as observed during present work with coal and biomass firing in the fluidised bed.

The fuel into the fluidised bed during this study is fed from a height of about 38cm from the top of the bed, so that volatiles may have been released around or under the feed point prior to burning in the freeboard [Grubor *et al.* 1987]. Burning of the volatiles was evidenced by large flames when observed through the observation port during the tests with coal as well as biomass. These flames appear to originate mainly from the burning of volatiles evolving from the fuel near or at the bed surface. When volatiles are completely burned the flame disappears and char is burned which was evidenced by glowing burning char particles when observed through the port.

Another factor which could have an influence on the freeboard temperature is the height above the bed at which the measurement is taken. The height of the containment tube (which contains the bed) of the fluidised bed combustor at Glamorgan University was restricted by the height of the roof. Therefore, the freeboard temperature was measured 0.44 m above the distribution plate (0.24 m above the static bed) while gas analyses were taken at 0.73 m above the distribution plate. Kuprianov *et al.* (2006) by co-firing rice husk and sugar cane bagasse found that their maximum temperature was observed at 1m height above the air distribution plate. Therefore it is possible that the freeboard temperature measured during the current tests was lower than the maximum which could have been achieved. Similar phenomena were observed by Armesto *et al.* (2002) during the combustion of rice husk and they have shown that the maximum temperature occurs between 40 and 60 cm above the distributor plate. However the fuel was fed into the bottom of the bed in these experiments. If the fuel had fed on the top of the bed the maximum temperature might have been recorded at a higher level in the combustor.

Freeboard height is very important in the current experiments as volatiles released from the fuel as well as unburned char continue to burn in this region. For a typical residence time of 1 – 2 s [Wiley, 1987] a velocity of 0.12 to 0.24 m/s is required for the volatiles to be completely burned over a length of 0.24m (which coincides with the point of freeboard

temperature measurement). As fluidising velocities used in virtually all the experiments were somewhat higher it is possible that the volatiles continued to burn well above the point of measurement which may have an effect on the results.

In contrast to coal, biomass fuel should be fed into the bed, not onto the bed, because of the higher reactivity of biomass in comparison to coal. In the present study all the solid fuels were fed above the bed and volatiles particularly from biomass may have been released even before the fuel reached the surface of the bed. In order to further illustrate this phenomenon Oka and Arsic (1983) mentioned that all the volatiles are not burned in the bed, even at optimum conditions, and some will burn in the freeboard. In these circumstances the temperature in the freeboard might be 200 °C higher than the bed temperature, assuming adiabatic furnace walls. As heat was lost through the walls of the containment tube in the present work, the freeboard temperature was lower than that would have been in the case of adiabatic process. It is also possible that the continued burning of the volatiles beyond the measurement point due to higher fluidising velocities may have resulted in the lower than anticipated temperatures in the freeboard. Moreover, Oka and Arsic (1983) pointed out that the difference in the temperature increases with decrease in the particle diameter. As small particles of coal (10 – 14mm) were used in this study, it could have an effect on the temperature profile. All these interdependent factors make it difficult to quantify the effect of individual parameters on the temperature profile. However, it can be concluded from the data analysis that the results of the bed and the freeboard temperatures obtained during this study are not unusual and are in agreement with the findings of the other researchers.

5.4 Co-Firing of Wood Chips with Coal:

One of the main objectives of the project is to investigate the co-firing of high moisture content biomass materials with coal as a support fuel so that tests were undertaken with wood chips with the normal moisture content of about 15% as well as with an artificially high value of 55% at different excess air levels. The tests were carried out at 10.3 – 13.6% O_2 and 9.5 – 12.8% O_2 for coal – 15% moisture chips and coal – 55% moisture chips blends (50/50, wt/wt), respectively. The 55% moisture level was selected on the basis of the fact that moisture content of the fresh wood is over 50% (w.b) and this was the maximum moisture absorbed by the chips when soaked in water for few days. From now on coal-15% moisture

chips and coal-55% moisture chips blends will be represented as 15%M and 55%M, respectively.

The wood chips used for the tests were provided by South Wales Wood Recycling Limited, Bridgend and were then sieved to get a size suitable for the screw feeder. The Size distribution of the "original" wood chips is given in Table 5.6. The chips were fed through the screw feeder to determine a suitable size which can be fed into the fluidised bed. It was found that 6 – 10 mm size chips were suitable but the feeder was jammed when wood chips with a larger size were fed. However, as can be seen from the table, 6 – 10 mm size chips were only 17% (by mass) of the total chips. Consequently the company was requested to supply smaller size "crushed" wood chips, the size distribution of which is given in the lower part of Table 5.6. As can be seen from the table, the crushed wood chips of 6 – 10mm size are now 41% of the total weight, almost 2.5 times of that was found in the original chips.

Table 5.6: Size distribution of Wood Chips

Size (mm)	%	Screw feeding observations
Original wood chips size distribution		
<6	7	Very small size, mostly dust
6 – 10	17	Flowing though the feeder but inconsistently
10 – 20	53	Feeder jammed
>20	23	Very big size
Crushed wood chips size distribution		
<6	33	Very small size, mostly dust
6 – 10	41	Flowing though the feeder but inconsistently
10 – 14	22	Feeder jammed
>14	4	Oversize

Particle dimensions and particle size distribution determines the appropriate feeding system and the combustion technology. As mentioned earlier although the size of the wood chips which could flow through the screw conveyor was typicallly 6 – 10mm the feed flow rate was not necessarily consistent. However, when the chips were mixed with coal the flow through

the screw conveyor was found to be improved and the flow rate was smooth and more consistent.

As the fuel goes into the bed its moisture is vaporised by using the energy generated by the process of combustion. Thus, lower energy is available to raise the temperature of the bed and this may slow the combustion process [Sjaak and Jaap, 2008]. Change in the moisture content of the fuel changes its bulk density as well as the energy density, see Table 5.7. This influences the combustion process as well as the control of the fuel feeding system. Thus the fuel feed rate is different for different moisture contents for a given power input. Although theoretical air requirement per kg of fuel decreases with increase in moisture content, it increases per unit of energy. Stoichiometric air requirement for the wood chips at 15% moisture content is 4.8 Nm^3/kg of fuel (5.8 kg air/kg fuel). When the moisture content is increased to 55% the stoichiometric air requirement is decreased to 2.6 Nm^3/kg of fuel (3.1 kg air/kg fuel). Stoichiometric air requirement per unit energy is 0.4 and 0.48 kg of air/MJ for 15% and 55% moisture wood chips, respectively. For 15%M blend stoichiometric air requirement is 6.4 Nm^3/kg fuel (7.7 kg air/kg fuel) and for 55%M blend it is 5.3 Nm^3/kg (6.4 kg air/kg fuel). This translates into a stoichiometric air requirement of 0.35kg of air/MJ for both 15%M and 55%M blends. Thus at the same excess air level the fluidising velocity for both of the blends should be almost the same. However, it should also be noted that fuel moisture evaporates during combustion process and becomes part of flue gas which may result in increase in fluidising velocity. High fluidising velocity may result in increased elutriation of unburned char and thus lower temperatures.

De-volatilisation of wood starts at 473 K and the rate of de-volatilisation increases with an increase in temperature. At 673 K most of the volatiles are gone and the de-volatilisation rate decreases rapidly [Sjaak and Jaap, 2008]. With high moisture content fuels, a higher amount of energy is used in evaporating water and less is available to be transferred to the bed and to raise the temperature of the char particles [Oka and Arsic, 1983]. When the temperature of the char particles is lower, the bed temperature drops. The presence of moisture cools the bed so that specific bed and freeboard temperatures can be achieved at lower excess air levels (lower oxygen concentrations in the dry combustion products). Due to the presence of higher amount of moisture, it is expected that the 55%M blend results in lower temperature than 15%M blend.

Table 5.7: Energy density of different fuels

	Air/Fuel	NCV	Bulk density	st.air/NCV	Energy density
	kg/kg	MJ/kg	kg/m^3	kg air/MJ	MJ/m^3
Coal	9.6	30	710	0.32	21300
Pellets	5.4	16.8	680	0.32	11424
Chips 15% Moisture	5.8	14.5	220	0.40	3190
Chips 55% Moisture	3.1	6.5	420	0.48	2730
15%M Blend	7.7	22.3	465	0.35	10370
55%M Blend	6.4	18.3	565	0.35	10340
Pressed pulp	1.8	3.2	480	0.56	1536

Excess air is used to maintain fluidised bed at a set temperature. Bed temperature increases if the excess air is decreased, and vice versa. When bed is cooled by other means, less excess air is required to maintain the bed temperature. Thus with higher moisture content fuels same bed temperature can be achieved at lower excess air levels.

Analysis of the blends of coal-chips on as received, dry and dry ash free basis are given in Table 5.8. The table shows that 55%M blend has considerably higher moisture content (30.3%) about 2.6 times than that of the 15%M blend (10.3%). The effect of moisture content on bed temperature is clearly demonstrated in Figure 5.16 which plots bed and freeboard temperatures Vs. O_2 (%) for a net thermal input of 15kW for both 15%M and 55%M blends. The figure shows that the bed and freeboard temperatures in the case of 15%M blend are higher than 55%M blend due to higher calorific value and lower moisture content of the former. Also it is clear from the figure that the bed and freeboard temperatures approach each other to some extent at higher excess air levels due to increased over bed burning. Both of the blends are showing similar behaviour.

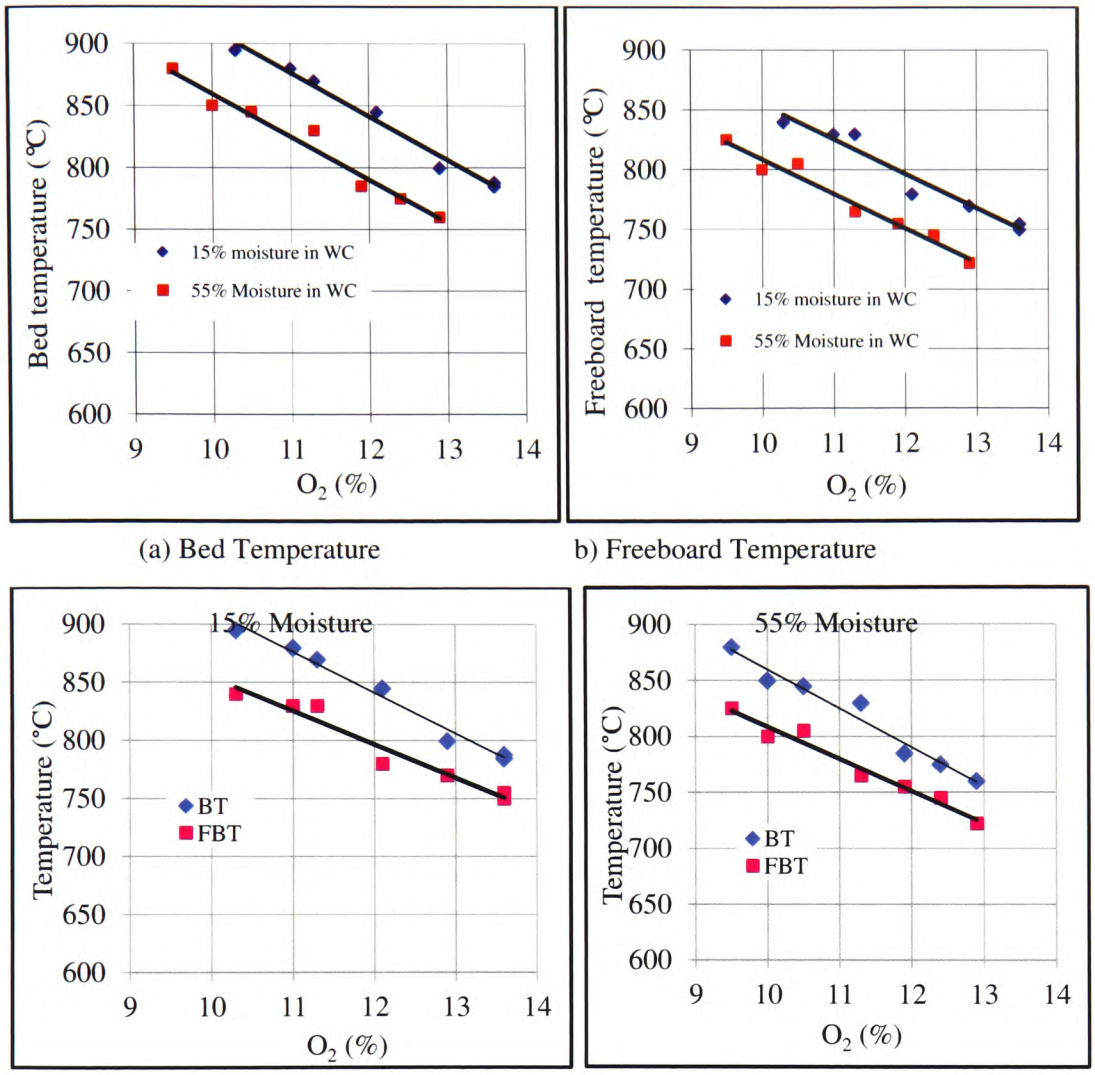
The figure 5.16 (a) and (b) also showsthat bed temperatures for the case of 55%M blend are around 50 °C lower than those for 15%M blend. This is perhaps due to the cooling effect of

higher moisture content of the 55%M blend. For example at 11% O_2 bed temperature with 55% moisture chips is 825 °C while with 15% moisture chips it is 875 °C. A bed temperature of 850 °C is achieved with 15%M blend at 11.7% O_2 (122% excess air) but with 55%M blend the temperature is achieved at around 10.2% O_2 (92% excess air) in the flue gas which is equivalent to 30% reduction in excess air.

Table 5.8: Analysis of Coal-Chips blends on as received, dry and DAF basis

	Original analysis		Dry Basis		DAF Basis	
	15%M blend	55%M blend	15%M blend	55%M blend	15%M blend	55%M blend
Carbon (%)	57.6	48	64.07	68.67	67.13	72.07
Hydrogen (%)	5.7	4	6.34	5.72	6.64	6.01
Oxygen (%)	19.4	11.9	21.58	17.02	22.61	17.87
Nitrogen (%)	1.3	1.1	1.45	1.57	1.52	1.65
Sulphur (%)	1	1	1.11	1.43	1.17	1.50
Chlorine (%)	0.8	0.6	0.89	0.86	0.93	0.90
Ash (%)	4.1	3.3	4.56	4.72		
Moisture (%)	10.3	30.3				
NCV (MJ/kg)	22.3	18.3				
GCV (MJ/kg)	23.8	19.9				
Air/Fuel (kg/kg)	7.7	6.4				

The same phenomenon was observed by Kuprianov *et al.* (2010) that an increase in fuel moisture content lowers O_2 level if the rest of the parameters are kept constant, an apparent effect of excess air. The evaporation of the water compensates for the cooling effect of the additional excess air. In addition to this effect, the presence of large quantities of moisture in the bed may act as a "barrier" for mixing of oxygen and the fuel particles so inhibiting combustion and hence lowering the bed temperature.



(a) Bed Temperature b) Freeboard Temperature

(c) 15% Moisture (d) 55% Moisture

Figure 5.16: Bed and freeboard Temperatures with 50/50 Coal-Wood Chips Blends

The effect of fuel moisture on the temperature profile was also observed by Patumsawad and Cliffe, (2002) by burning MSW and blend of MSW and vegetable waste. They found that the freeboard temperature of the blend was higher than that of MSW alone showing that vegetable waste burnt in the bed resulting in higher bed temperatures while dried MSW tended to burn above the bed. However, during tests with different moisture content wood chips the phenomena was not observed and both BT and FBT_1 are found to be lower for higher moisture for a specific thermal input and excess air level.

Patumsawad and Cliffe, (2002) found that freeboard temperatures were higher for 15% moisture blend of MSW and vegetable waste than those for MSW at the same moisture content. They found that freeboard temperature (850 °C) was almost 200 °C higher than the bed temperature (640 °C) for simulated MSW with 5% moisture due to burning of volatile matter (65%) above the bed. Increase in moisture content increases de-volatilisation time so that the fuel has more time to burn in the bed. Due to this reason the bed temperature (750 °C) at 10% moisture was higher than that at 5% moisture (640 °C). However bed temperature (710 °C) at 15% moisture was lower than that at 10% moisture due to the effect of increased moisture. MSW with 20% moisture resulted in the lowest bed temperature of 600 °C and this was unstable. Freeboard temperature at this moisture was 50 °C higher than the bed temperature. Because moisture content in present tests was very much higher than Patumsawad and Cliffe (2002) it is not possible to compare the results directly.

Kuprianov *et al.* (2010) also observed similar lower temperatures at higher fuel moisture content. Their Maximum temperature with as received rice husk (8.4% moisture) was 900 °C which reduced to 800 °C when the fuel moisture content was increased to 25%. They also found lower temperatures at all the measurement locations in the combustor with increase in fuel moisture content. This is in exact agreement with the findings of the present study. However, Shao *et al.* (2010), by co-firing high moisture peat and pine pellets in a fluidised bed combustor observed that higher moisture fuels produced higher and more uniform temperatures.

Figure 5.17 shows plots of the combustion efficiency of the blends of coal-chips against O_2% in the flue gas. It can be seen from the figure that the efficiency is higher when measured at FBT_1 than that at BT, in both cases due to burning of volatiles above the bed. Comparison of the plots shows that in the case of 55%M blend efficiencies at BT and FBT_1 are lower than 15%M blend due to higher moisture content of the former. It is also clear from the figure that despite the lower efficiencies the effect of excess air on the efficiency is more pronounced in the case of 55%M blend with a much more marked increase with oxygen. This relative increase is due to increased moisture content of the blend which delays evolution of the volatiles so that they burn more readily in the vicinity of the bed. Also due to higher moisture content ignition is delayed and char stays in the bed longer to raise its temperature.

This is clearly shown in Figure 5.17 which illustrates that the overall fluidised bed efficiencies with normal wood chips (15% M) are in the range from about 79 to 89% and are 68 to 80% with the higher moisture content material. Although the efficiency increases with oxygen content and excess air level this appears to be in conflict with the theoretical efficiency which decreases with increasing excess air. This is shown in Figure 5.18 whichshows a plot of theoretical efficiency Vs. O_2 concentration in flue gas for wood [Sjaak and Jaap, 2008]. The efficiency is calculated on the basis of 55% moisture content of wood chips and GCV of 20.3 MJ/kg and presumably assumes that the distribution of combustion is unaffected by the excess air level. It can be seen from the figure that efficiency decreases from 89% at 3% O_2 to 79.5% at 14% O_2, a drop of around 10%.

The opposite trend in the efficiency may be due to method of calculation. In this thesis the efficiency calculated is not combustion efficiency but self defined "fluidised bed efficiency" as illustrated in Appendix C. The efficiency represents the performance of the fluidised bed to produce hot combustion products to be used in the subsequent drying process. Thus direct comparison of Figures 5.17 and 5.18 may not be appropriate.

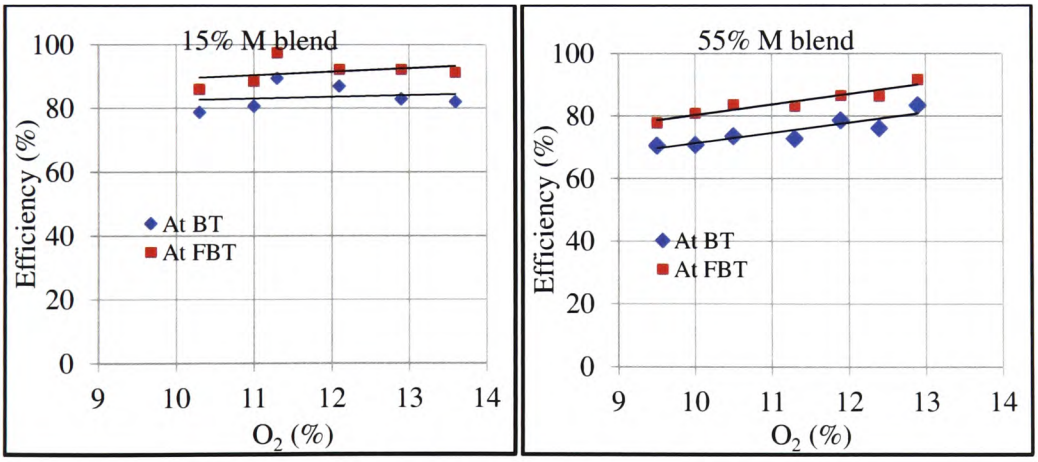


Figure 5.17: Efficiency Vs. O_2 for 15%M and 55%M blends

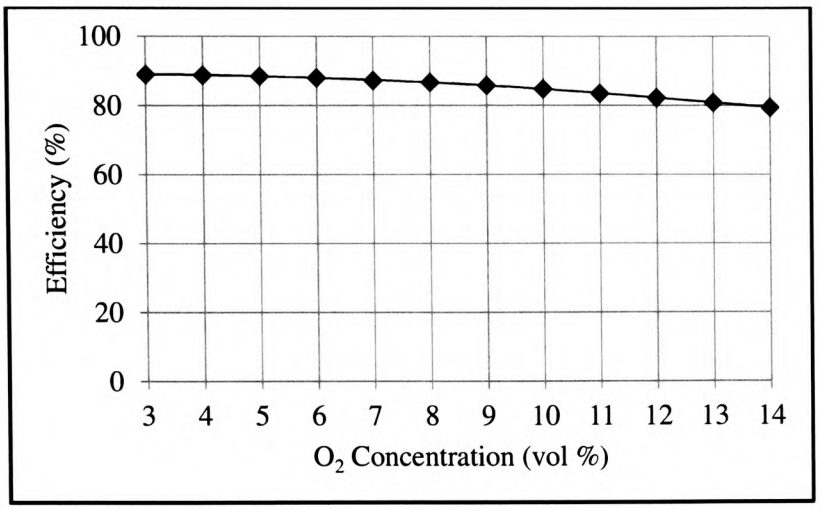


Figure 5.18: Influence of Excess air on combustion efficiency
(Wood chips, moisture of 55% and GCV of 20.3 MJ/kg, dry basis) [Sjaak and Jaap, 2008]

Overall this section of the thesis has demonstrated the effects of moisture content of the co-fired biomass material on the behaviour of the coal-biomass blend and provided good basis for co-firing tests with coal and pulp blends which is the main fuel to be tested. Hence in the following paragraphs co-firing tests of coal and pulp blends are discussed.

5.5 Co-Firing of Pressed Sugar Beet Pulp with Coal:

A financial analysis which was undertaken in a parallel study concluded that co-firing of pressed sugar beet pulp with coal may be an attractive financial proposition on the fluidised bed combustor at the Cantley factory of British Sugar despite potential problems in fuel handling. Therefore, tests have been performed by co-firing pressed pulp and Thoresby coal at different mixing ratios, power inputs and excess air levels. Compositions of the coa-pressed pulp blends tested are 50/50, 60/40 and 70/30 by mass in the thermal input range of 11.8 to 19.7 kW at flue gas O_2 concentrations ranging from 5 to 12.8%. The results of the experiments with coal-pulp blends are summarised and compared with coal only firing in Table 5.9.

Before discussing the results obtained during the experiments it is necessary to explain a few factors associated with charging of the blended fuel which could influence the accuracy of the

final results. These include the following which could have resulted in variations of the fuel flow rate and moisture content of the blended material which could have made it more difficult to burn in an efficient way.

1. The coal and pressed pulp was mixed manually, so that variations in the blended fuel composition are expected.
2. The blend was mixed and charged into the feed hopper by a polythene container so that the heavier coal particles can separate and tend to concentrate at the bottom of the hopper.
3. The coal-pressed pulp blend tends to bridge in the hopper. Despite efforts to break this bridge in the feed hopper from time to time to ensure that the feed flow was as uniform as possible, it is possible that the heavier coal particles could have settled out to the bottom of the hopper.

All these factors make the uniform feed of the blend into the bed difficult. This could have an effect on the results obtained during these tests.

Table 5.9: Results of Coal and Pressed Pulp tests

	50/50	60/40	70/30	100/0
Thermal input (kW)	11.8 – 14.2	13.3 – 19.7	12.7 – 14.6	8.7 – 18.2
O_2 in flue gas (%)	5 – 11.5	7 – 12.1	8.9 – 12.8	9.7 – 14.5
Efficiency at BT (%)	58 – 83	59 – 83	67 – 93	72.5 – 92.3
Efficiency at FBT_1 (%)	71 – 97	69 – 94	76 – 100	80.5 – 99
Fluidising velocity (%)	1.6 – 2.6	1.9 – 2.4	1.8 – 2.3	1.9 – 3.1

It was observed that pressed pulp was not able to flow consistently through the screw feeder due to its very high moisture content and sticky nature. However, when it was mixed with coal the blend was able to flow through the screw feeder more smoothly and no problems were observed apart from bridging of the material in the feed hopper. A similar feeding problem was also observed by Patumsawad and Cliffe (2002) who found that increasing moisture content caused simulated MSW particles to stick together and feeding was difficult.

Kuprianov *et al* (2006) also observed feeding problems with sugar cane bagasse due to its high moisture content and relatively large particle size.

The pulp has a typical moisture content of about 71% and hence a very low net calorific value of 3.20 MJ/kg. Consequently even with a 50/50 blend (by mass) of coal and pressed pulp (the highest proportion of pulp that can be successfully tested in the pilot scale facility) most of the thermal input (about 90%) arises from the combustion of coal, see Table 5.10 which shows analysis of all the three coal-pulp blends tested. It can be seen from the table that the calorific value of the coal-PP blends is in the range of around 17 to 22 MJ/kg which is in the same range as that reported by Sjaak and Jaap, (2008) for biomass materials.

For each of the three blends (i.e. 70/30, 60/40, and 50/50 coal-pulp) the bed and freeboard temperatures decreased as the excess air (oxygen) level was increased, see for example Figure 5.19 which plots bed temperature and freeboard temperatures as a function of O_2 % in the flue gas for 50/50 coal-PP blend at 14.2 kW. It can be observed from the figure that the bed and freeboard temperatures approach each other as O_2 concentration in the flue gas increases and become equal at a value of 820 °C and at about 10.4% O_2 concentration. In the case of coal only firing, at similar thermal input, the condition was achieved at 750 °C and at about 14.6% O_2 (Figure is not shown to keep data analysis simple). The reason for freeboard temperature becoming equal to bed temperature in the case of 50/50 coal-pulp blend firing at lower excess air level than coal only firing may be that during co-firing more over bed burning takes place due to the higher volatiles content of the pressed pulp. Volatiles content (percentage of combustibles) of coal is typically 38.2% while that of the PP is very much higher at about 99.6%. A 50/50 blend of coal and PP therefore has a volatile content of about 52.5%. Although volatiles content of pressed pulp is 2.6 times that of coal, that of 50/50 blend of coal and pressed pulp is only 1.4 times. This is due to very low dry matter contribution of pressed pulp. The phenomenon of high overbed burning has also been demonstrated during the combustion of other coal/biomass fuels.

Bed and freeboard temperature profiles for 60/40 and 70/30 coal-PP blends against O_2 concentration in flue gas are shown in Figures 5.20 and 5.21, respectively. For all the three blends data is plotted for almost same thermal input. The figures show similar trend as shown in Figure 5.19 that both bed and freeboard temperatures decrease with increase in O_2

concentration but at different rates. Bed temperature decreases at a faster rate as compared to freeboard temperature and at a certain excess air level freeboard temperature becomes higher than bed temperature. Comparison of figures show that for 50/50 blend freeboard temperature becomes higher than bed temperature quicker as compared to 60/40 and 70/30 blends. For 60/40 and 70/30 blends the condition occurs at 10.9% O_2 as compared to 10.4% for 50/50 blend. It should also be noted that the conditions occurs at 820 °C for 50/50 and 60/40 blend but at 840 °C for 70/30 blend. The occurrence of the condition earlier for blends with higher PP proportion may be due to increased overbed burning of PP.

Comparison of bed temperatures for all the three blends against O_2 concentration is shown in Figure 5.22. The figure shows that for a particular excess air level, bed temperature for 50/50 blend is the lowest followed by 60/40 and 70/30 blends. For example, at 10% O_2 in the flue gas stable bed temperature for 50/50 blend is 830 °C while for 60/40 and 70/30 blends it is 845 and 860 °C, respectively. Similarly, a specific bed temperature is achieved at the lowest excess levels for 50/50 blends followed by 60/40 and 70/30 blends, respectively. For example, a bed temperature of 850 °C can be achieved at 9.3%, 9.9% and 10.5% O_2 for 50/50, 60/40 and 70/30 blends, respectively. This is due to increased moisture content of the blend with increase in blending ratio of pulp which cools the bed down and a required bed temperature is achieved at lower excess air levels.

Freeboard temperatures for the coal-pulp blends are compared in Figure 5.23. The figure plots freeboard temperature against O_2 in the flue gas. The plot shows that for a specific excess air level freeboard temperature for the 50/50 blend is the lowest followed by 60/40 and 70/30 blends, respectively. It can be observed from the figure that slopes of the freeboard temperature profiles are different for all the three blends. The profile is the steepest for 70/30 blend followed by 60/40 and 50/50 blends, respectively. This may be due to increased overbed burning with increase in blending ratio of pulp in the blend.

The higher freeboard temperature (relative to the bed temperature) at high excess air levels for all the coal-PP blends tested suggests that considerable overbed burning may occur as a result of the high levels of volatiles in the pulp. Nevertheless it is difficult to estimate the proportion of the pulp which burns above the bed because of scatter in the data from fuel mix to fuel mix, uncertainties in the calorific value of the pulp, and the relatively low proportion

of the thermal input contributed by this material. However analysis of the results for the three blends which were tested suggests that at least 50% of the pulp burns above the bed and that this would be a reasonable value to use when considering the behaviour of pressed pulp combustion in the fluidised bed of the full scale plant.

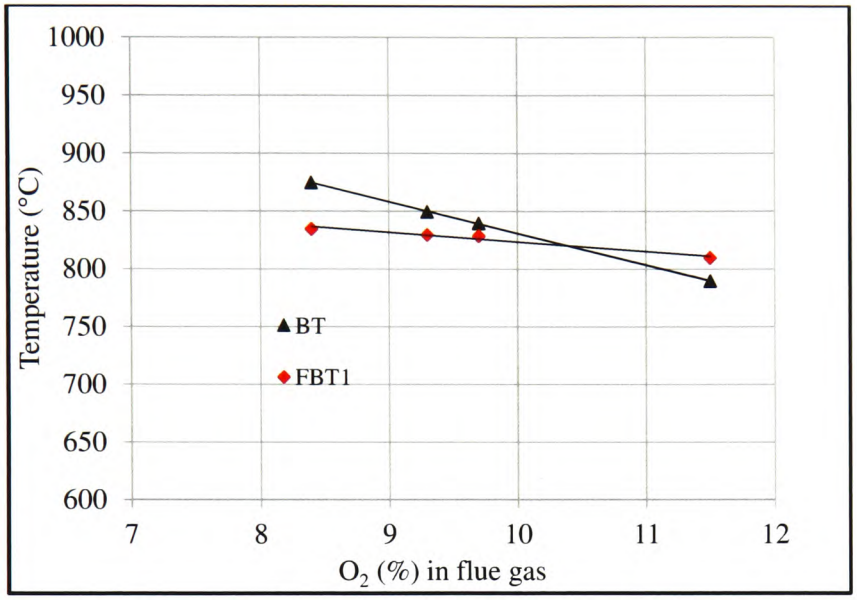


Figure 5.19: Bed and Freeboard Temperatures when Co-Firing a 50/50 Coal-Pulp blend

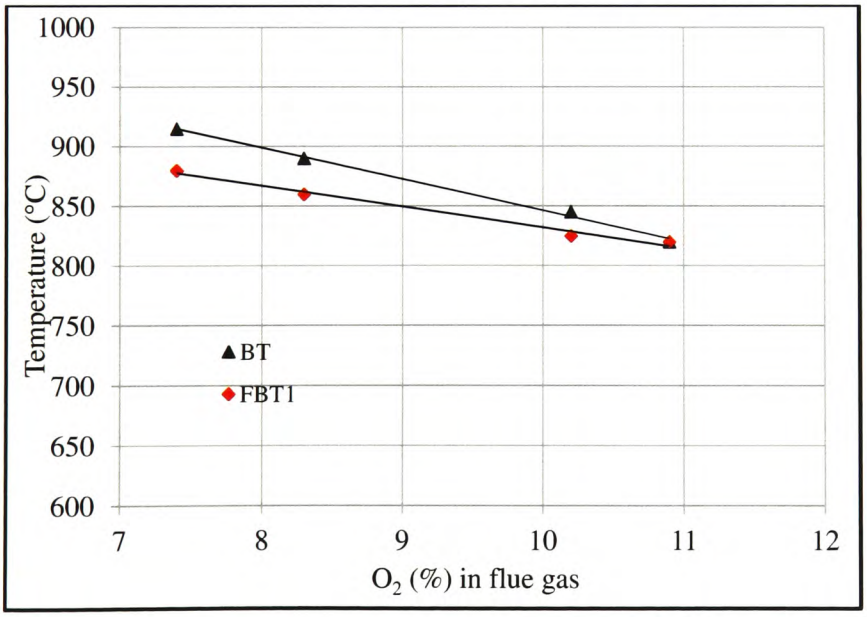


Figure 5.20: Bed and Freeboard Temperatures when Co-Firing a 60/40 Coal-Pulp blend (14.7 kW)

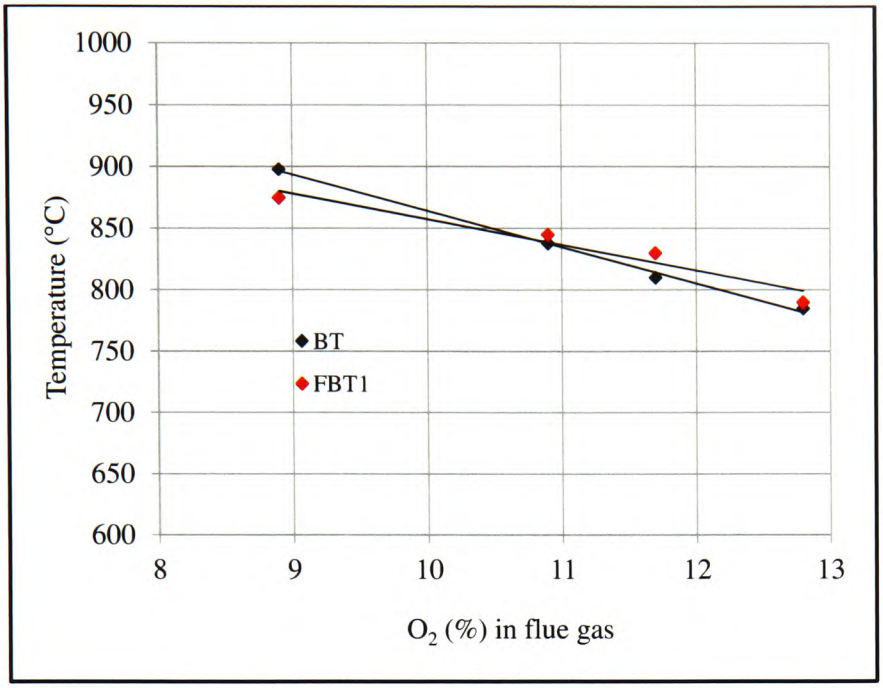


Figure 5.21: Bed and Freeboard Temperatures when Co-Firing a 70/30 Coal-Pulp blend

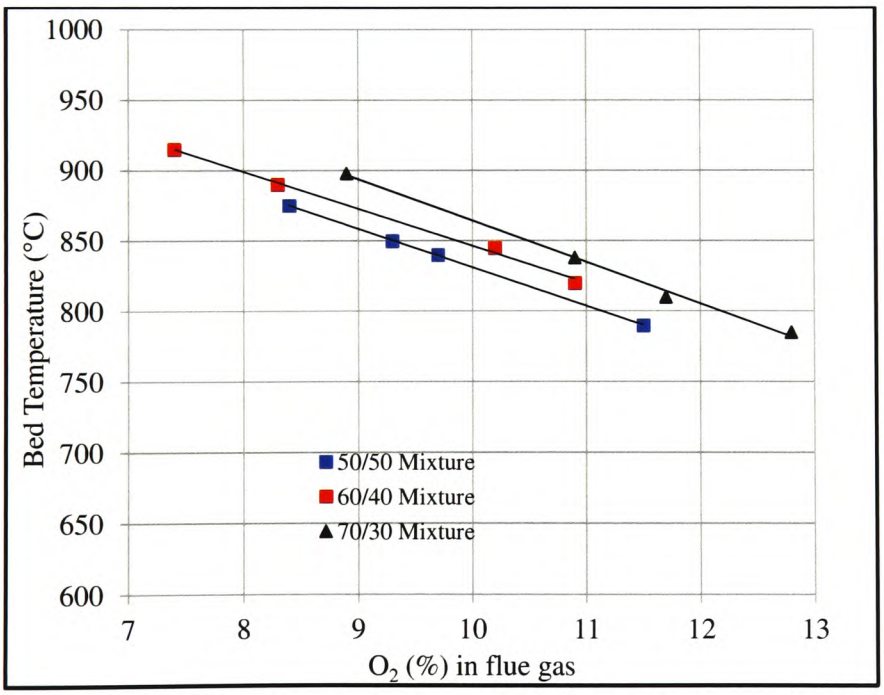


Figure 5.22: Bed temperature comparison for Coal-Pulp blends

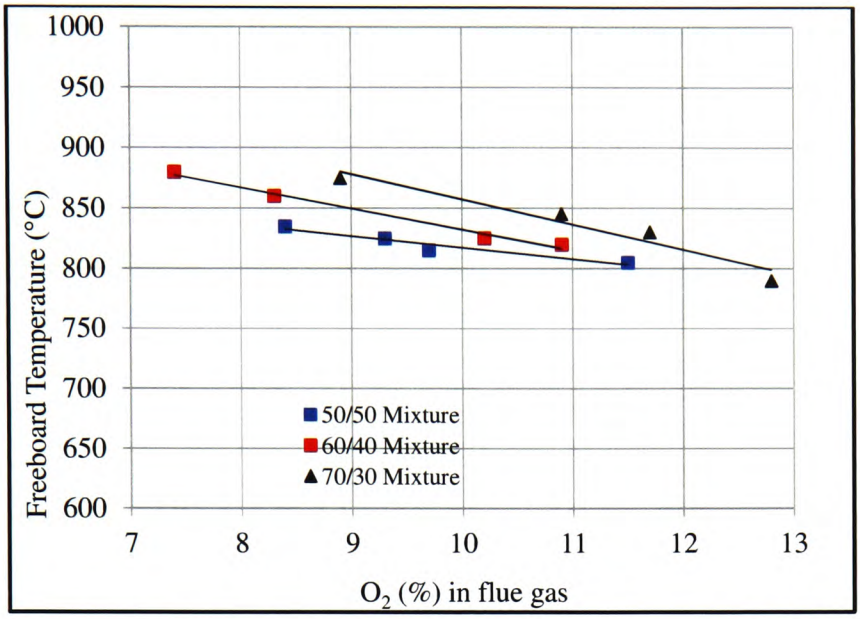


Figure 5.23: Freeboard temperature comparison for Coal-Pulp blends

Table 5.11 gives the dependence of bed and freeboard temperatures on O_2 at different concentrations in the flue gas. The table shows the O_2% level at which bed and freeboard temperatures become equal. It can be seen from the table that BT and FBT for coal become equal at a lower temperature and higher O_2 level than those for coal and PP blends. The temperature is very much lower for coal than that for blends. This is probably due to higher O_2 level (excess air) for coal than blends which could have dilution effect to lower the temperatures. However, in the case of blends the temperature is increasing with increase in coal proportion in the blend. This could be due to the relatively low excess air used in the case of blends as compared to coal. As blends have higher moisture than coal it is also possible that this results in the fuel staying longer in the bed and burning there and as a result causing the bed temperatures to go up.

Table 5.10: Analysis of Coal-Pulp Blends (as received)

	Coal	Pressed pulp	50/50 blend	60/40 blend	70/30 blend
Carbon (%) AR	74.42	14.1	44.3	50.3	56.3
Hydrogen (%) AR	4.06	1.8	2.93	3.16	3.38
Oxygen (%) AR	6.97	10.9	8.94	8.5	8.1
Nitrogen (%) AR	1.62	0.14	0.88	1	1.2
Sulphur (%) AR	2.01	0.14	1.08	1.26	1.45
Chlorine (%) AR	0.63	0	0.32	0.38	0.44
Moisture (%) AR	5.6	71	38.3	31.76	25.22
Ash (%) AR	4.9	2	3.45	3.74	4.03
Volatiles (%) AR	34.2	25.1	29.7	30.6	31.5
Fixed carbon (%) AR	55.3	1.9	27.4	32.4	37.5
Ash (%) Dry	5.19	6.9	5.7	5.6	5.52
Volatiles (%) Dry	36.23	86.55	49.05	45.85	43.13
Fixed carbon (%) Dry	58.58	6.55	45.25	48.55	51.35
C (%, DAF)	82.96	52.07	75.79	77.78	79.42
H (%, DAF)	4.53	6.65	5.02	4.88	4.77
O (%, DAF)	7.77	40.25	15.3	13.21	11.49
N (%, DAF)	1.81	0.52	1.51	1.59	1.66
S (%, DAF)	2.24	0.52	1.84	1.95	2.04
St. Air (Nm^3/kg of fuel)	8.01	1.5	4.76	5.41	6.06
A/F ratio (kg/kg)	9.6	1.8	5.7	6.48	7.26
CV Net, (MJ/kg)	30.1	3.2	16.65	19.34	22.03
Air/NCV (kg/MJ)	0.32	0.56	0.34	0.335	0.33
Contribution					
Coal (MJ/kg)	30.1	0	15.05	18.06	21.07
PP (MJ/kg)	0	3.2	1.6	1.28	0.96
Coal (%)	100	0	90.4	93.4	95.6
Pressed pulp (%)	0	100	9.6	6.6	4.4

Table 5.11: Comparison of BT and FBT for Coal-Pulp blends

	50/50 blend	60/40 blend	70/30 blend	Coal
Input (kW)	14.2	14.7	14.6	14.4
O_2 and T at which BT and FBT_1 cross				
O_2 (%)	10.4	10.9	10.9	14.6
Temperature (°C)	820	820	840	750
10%O_2				
BT (°C)	830	848	865	937
FBT_1 (°C)	825	830	860	860
11% O_2				
BT (°C)	805	818	840	890
FBT_1 (°C)	815	819	840	835

Above comparison does not clarify the influence of blending ratio on bed and freedoard temperatures due to the involvement of additional parameter i.e. excess air which also has an effect on the temperatures. Therefore, the table also shows the bed and freeboard temperatures for coal and blends at fixed O_2 levels in the flue gas. It can be seen from the figure that at 10% O_2, BT is considerably higher than FBT_1 for coal. For coal-PP blends these temperatures are closer which shows that the pressed pulp portion tends to burn over the bed. It can be seen from the table that at 10% O_2 bed temperature is higher than freeboard temperature for all the three blends while at 11% O_2 it is vice versa. Thus increase in excess air increases the amount of over bed burning.

The fluidised bed efficiency for 50/50 coal-PP blend at 14.2kW thermal input is plotted in Figure 5.24. The figure shows a plot of efficiency vs. O_2 as measured at BT and FBT_1. It can be seen that the efficiency at FBT_1 is consistently higher than that at BT as a result of the overbed burning of volatiles from PP. It is also clear from the figure that the efficiency increased with O_2 (%) in the flue gas (i.e. the excess air level). Although the efficiency at BT is relatively unaffected by excess air, that at FBT_1 is increased by about 8%. This also shows

the effect of increased over bed burning with increasing excess air. Figures 5.25 and 5.26 show similar plots for 60/40 and 70/30 blends. The figures show similar trend as observed in Figure 5.24 for 50/50 blend. For all the three blends efficiencies are in the same range although the effect of overbed burning on freeboard efficiency is clear in all the cases. The range of efficiencies for all the tests conducted is given previously in Table 5.9. The data shows that the efficiency decreases with increase in pulp proportion in the blend due to increase in moisture although due to scatter in the data, it is difficult to make a clear distinction. Moreover, behaviour of 50/50 and 60/40 blends is close to each other while that of 70/30 is little bit different which shows higher efficiencies at both BT and FBT_1 as compared to the other two blends and seems to show intermediate behaviour between coal and 60/40 and 50/50 blends.

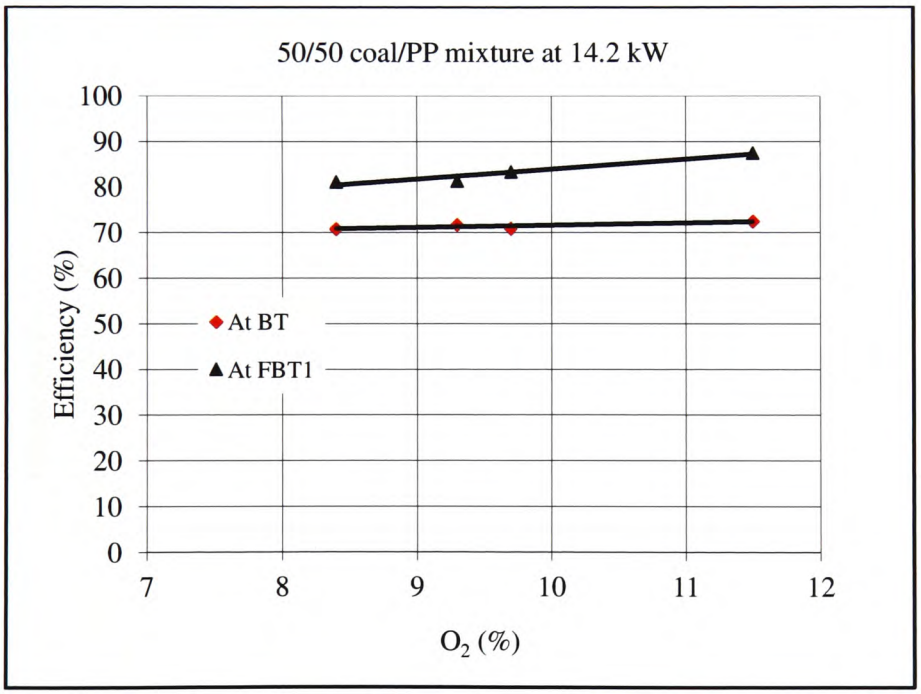


Figure 5.24: Efficiency Vs. O_2 for 50/50 Coal-Pulp blend

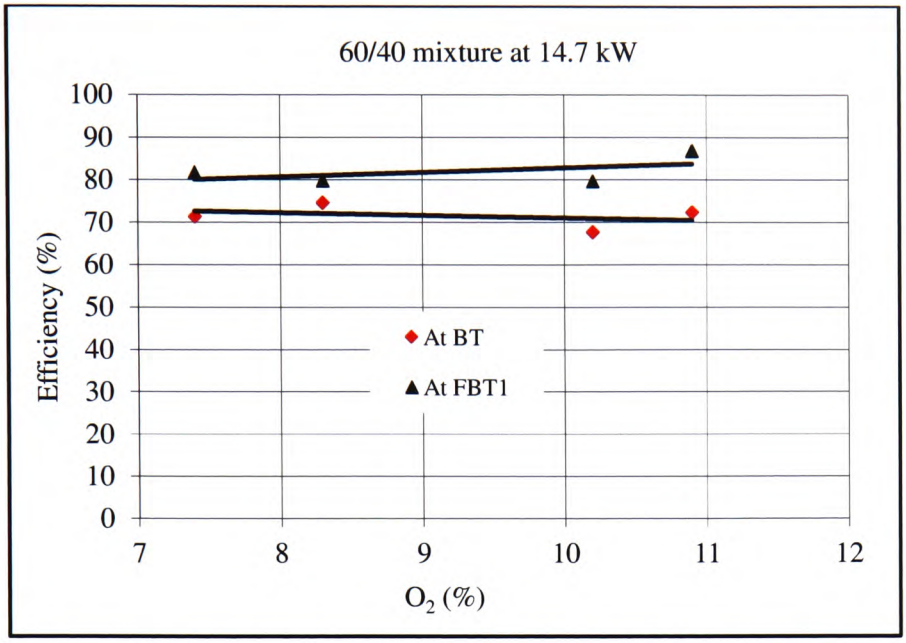


Figure 5.25: Efficiency Vs. O_2 for 60/40 Coal-Pulp blend

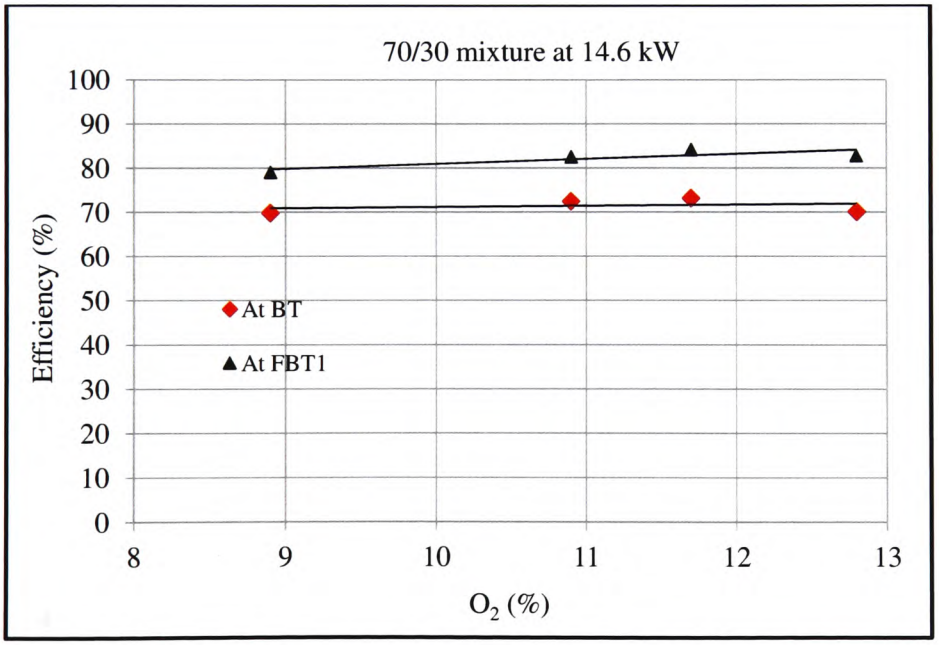


Figure 5.26: Efficiency Vs. O_2 for 70/30 Coal-Pulp blend

So far in this chapter data acquired during co-firing tests is analysed. Following paragraphs discusses the influence of fuel moistureon the performance of the fluidised bed during combustion of coal and PP blends. The effect of moisture on temperature profiles, excess air requirement and efficiency is discussed.

5.6 The Effect of Fuel Moisture on the Performance of the Coal-ulp blends:

So far in this chapter, results of experimental data with different fuels and their blends is presented and analysed. The effect of fuel moisture on the performance of the fluidsed bed is analysedin the following paragraphs.

5.6.1 The Cooling Effect of Fuel moisture on excess air:

The variation of bed temperature with increasing oxygen level and hence excess air is presented in Figure 5.27 for coal and all the three blends of coal and pressed pulp at virtually constant net thermal input of approximately 14 kW. The data represented in the Figure is smoothed over the range of conditions tested. Generally as the proportion of the pressed pulp is increased the cooling effect of the additional moisture is also increased. Air supplied to practical combustion systems is well above stoichiometric. Thus, the combustion or adiabatic flame temperature is significantly reduced as some of the heat of the combustion process is used for heating up of the excess air. Consequently, when firing with high moisture fuel a fixed bed temperature can be maintained at a lower excess air (oxygen) level since "additional" air is not required to cool the bed. This reduction in the necessary air flow to maintain a fixed bed temperature can be seen more clearly in Figure 5.28 which plots, for a constant thermal input, the measured air flow to the fluidised bed against the proportion by mass of the pressed pulp in the blended fuel at particular fixed bed temperatures.

A blend of 70/30 coal-pulp has around 27% lower CV and 350% higher moisture than coal, so the excess air required to get a fixed bed temperature should have been drastically reduced when firing 70/30 coal-pulp blend as compared to coal alone. However, the data shows that there is little reduction in excess air (only 1 – 2%) over the conditions tested when fuel is switched from coal to 70/30 coal-pulp blend. Thus, the effect of fuel moisture on the reduction of excess air when firing 70/30 coal-pulp blend is not significant. This may be due

to the dominance of coal in the blend which is contributing around 88% of the total dry matter and is contributing around 96% towards the total energy input from the blend. Thus blends of small proportions of pulp with coal can be co-fired with little effect on the performance of the combustor. This is in line with the findings of Howe and Divilio (1993) who assessed pilot and commercial experience on fluidised bed combustion and found that co-firing with 10 – 20% (weight basis) of secondary fuel is possible with minimal impact on performance and design.

However, when 60/40 coal-pulp blend is combusted reduction in excess air is significant although the change in moisture of fuel in this case is only 25% and change in energy value is 12%, as compared to 70/30 blend. The excess air requirement to get a bed temperature of 800 °C is reduced by around 10% as compared to 70/30 blend and around 11% as compared to coal. Thus the effect of moisture on the reduction of excess air is more for 60/40 blend (32% moisture) as compared to 70/30 blend (25% moisture). Similarly excess air requirement for getting a bed temperature of 850 °C is reduced by more than 11.4% as compared to 70/30 blend and by 12.5% as compared to coal. And excess air requirement for getting a bed temperature of 900 °C is reduced by more than 11.5% as compared to 70/30 blend and by 13.3% as compared to coal. In 60/40 blend dry matter contribution of coal is 83% and its energy contribution is 93%. Neither the energy contribution of coal nor the moisture content of the 60/40 blend is significantly changed as compared to 70/30 blend relative to change in these properties for 70/30 blend as compared to coal. Therefore, the significant changes in excess air requirement for 60/40 blend may be due to combined effect of increased moisture and reduced thermal input contribution by coal. This also suggests that there is a specific moisture content at which its effect on the bed cooling is significant.

For 50/50 blend increase in moisture is 21% and reduction in energy value is 14% as compared to 60/40 blend which is not very much different from the relative difference between 60/40 and 70/30 blends. In the case of 50/50 blend excess air is reduced by 5 – 9% as compared to 60/40 blend and 19 – 20% as compared to coal, with higher values at lower bed temperatures. The reduction is 9% at 800 °C and 5% at 900 °C as compared to 60/40 blend. This may be due to the reason that at higher temperature moisture is evaporated relatively quickly and fuel combustion rate increases which results in higher bed temperature and thus requirement of excess air for a fixed bed temperature is increased. At lower

temperature moisture stays longer in the bed which slows fuel burning rate which results in lower bed temperature. In order to increase the bed temperature air flow needs to be reduced so that higher reduction in excess air is observed at lower bed temperatures. Therefore, the reduction in air flow increases relatively sharply when PP proportion is increased to higher levels so that overall about 20% less air is required when the ratio of the pressed pulp is increased to 50%. The air spared by moisture (around 6.5 m^3/h) can be used to burn 4kW equivalent of more coal and thus can result in 30% improvement in throughput.

Similarly, the air flow which is required to maintain a constant overbed temperature is progressively reduced as the proportion of the pressed pulp is increased to these high levels, see Figure 5.29. These reductions in the required fluidising air flow rates will have a beneficial effect on the operation of the fluidised bed hot gas generator at Cantley since at present the flow rate of the fluidising gases and hence the amount of coal which can be burnt in the bed is limited by high pressure drops in the existing sparge pipe distributor [Garwood *et a.*, 2006]. The ability to operate with lower excess air levels due to the cooling effect of the pulp will enable the thermal input to the full sized plant to be increased. Moreover, the drying capacity of the combustion products will be increased by the presence of additional moisture, with a high specific heat, from the pressed pulp.

The discussion above concludes that the optimum blending ratio of Thoresby coal and pressed sugar beet pulp is 50/50 (wt/wt) as it is the maximum ratio which was successfully fired and that it gives maximum reduction in excess air requirement for a fixed bed temperature.

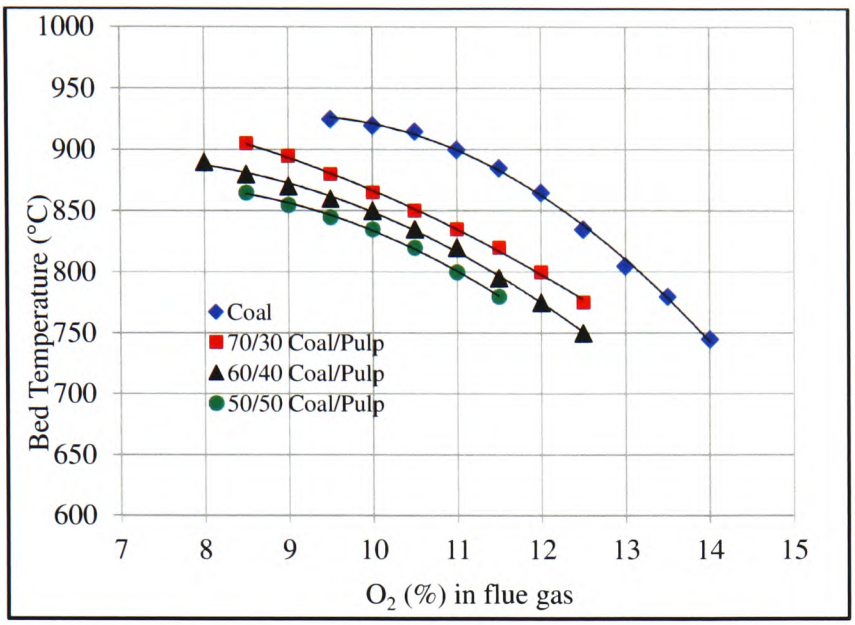


Figure 5.27: Bed Temperatures with Different Blends of Coal and Pressed Pulp

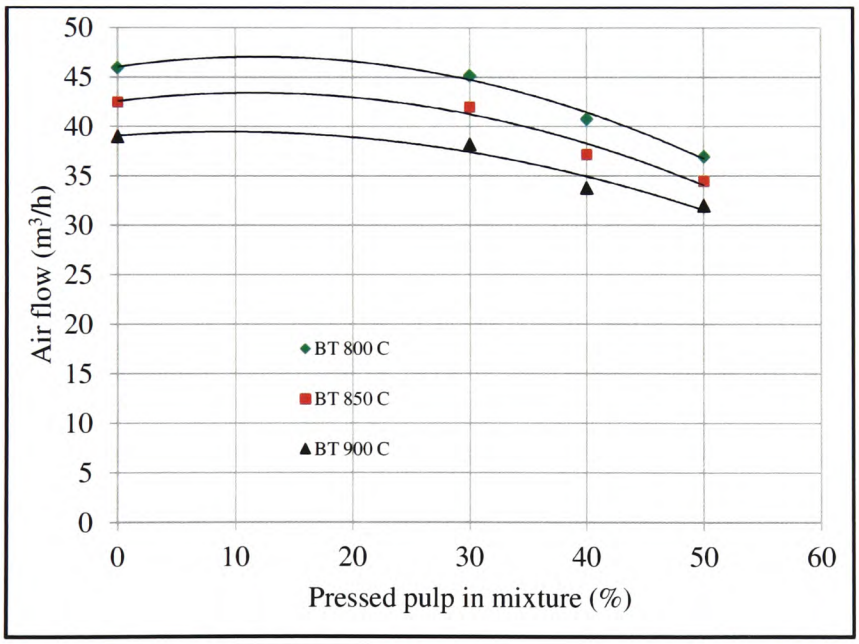


Figure 5.28: The Effect of Coal-Pulp Blend Proportions on the Overall Fluidising Air Flow rates required to achieve a Fixed Bed Temperature

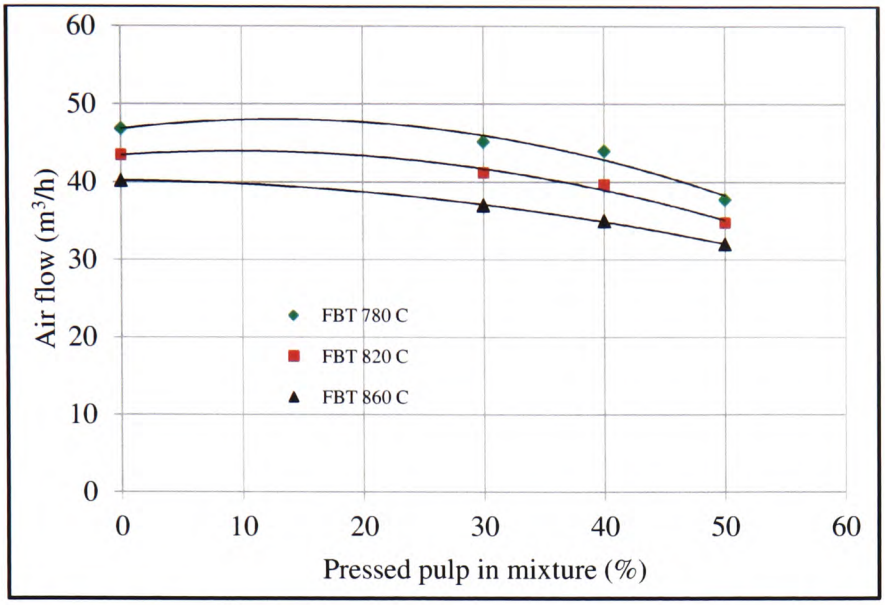


Figure 5.29: The Effect of Coal-Pulp Blend Proportions on the Overall Fluidising Air Flow rates required to achieve a Fixed Freeboard Temperature

5.6.2 The Effect of fuel moisture on the temperature profile in the bed:

Fuel moisture has a considerable effect on the temperature profile in the fluidised bed. As mentioned earlier, it was not possible to burn coal-pulp blend containing more than 50% pulp due to its very high moisture content (around 71%). The increase in moisture content reduces the calorific value of the fuel so that the energy released by combustion is not enough to sustain the process and the bed temperature drops to unsustainable limits.

Higher moisture contents result in lower temperatures in the fluidised bed as demonstrated previously by the experiments with coal and wood chips. The bed and freeboard temperatures with 55%M blend (30% moisture in blend) are found to be almost 50 °C lower than those with 15%M blend (10% moisture in blend).

The effect of moisture on bed and freeboard temperatures has also been demonstrated when co-firing coal and pressed pulp blends. The temperatures in the system decrease with an increase in proportion of the pressed pulp due to its very high moisture content contribution. Results show that there is a considerable drop in temperatures for 70/30 blend as compared to coal alone. This is due to considerable increase in moisture content, 25.2% for blend as

compared to 5.6% for coal. However, with 60/40 and 50/50 blends the difference in temperatures is not that significant due to relatively lower difference in moisture contents of the 60/40 and 50/50 blends having 31.8 and 38.3% moisture, respectively. However, in comparison to coal alone, 50/50 and 60/40 blends are more different than 70/30. Overall there is almost 30 °C difference in bed temperatures between 50/50 and 70/30 coal-pulp blends which is lower than what is observed during the combustion of coal-chips blends, possibly due to relatively lower moisture content variation in the former case.

It can be seen from Table 5.11 that at 10% and 11% O_2 in the flue gas bed temperature for the 50/50 blend is lower than 60/40 and 70/30 blend, possibly due to higher moisture content of the 50/50 blend. With increase in moisture content, the calorific value of the fuel drops which results in lower temperatures.

Adiabatic flame temperature is affected by excess air and moisture content of fuel. This is illustrated inFigure 5.30 [Sjjak and Jaap, 2008] by the theoretical effect of excess air and moisture content of fuel on adiabatic flame temperature for a representative fuel having 50% carbon, 6% hydrogen and 44% oxygen on dry ash free basis. The figure shows that adiabatic flame temperature decreases with increase in moisture content and excess air. With dry fuel (0% moisture) adiabatic flame temperature decreases from around 2100 °C at stoichiometric air to around 1250 °C at 100% excess air and to below 900 °C at 200% excess air. At stoichiometric condition adiabatic flame temperature decreases from around 2100 °C at 0% moisture to around 1500 °C at 50% moisture and decreases to about 750 °C at 50% moisture and 200% excess air.

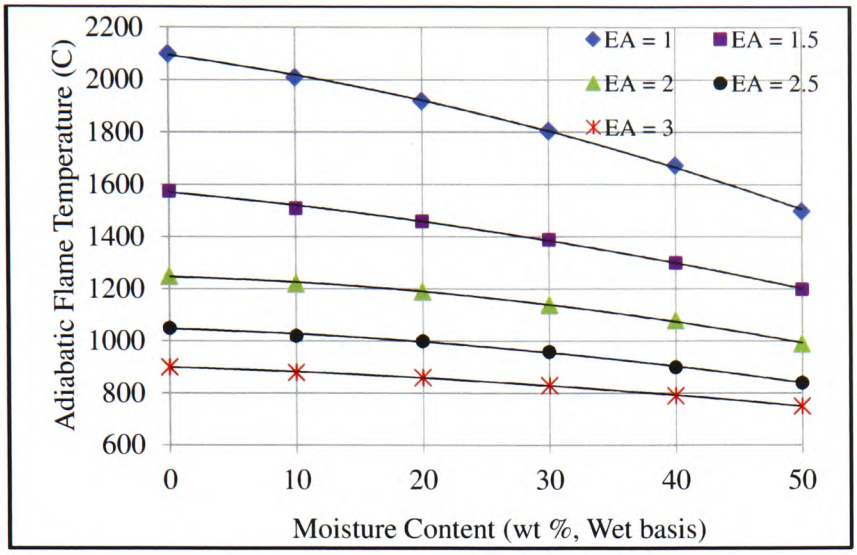


Figure 5.30: Adiabatic flame temperature as a function of moisture content and excess air ratio (EA) for a fuel with 50% C, 6% H and 44% O [Sjaak and Jaap, 2008]

The figure shows that at 150% excess air and 40% fuel moisture adiabatic flame temperature is around 900 °C which is in the range of fluidised bed operating temperature. Therefore, theoretically, under adiabatic conditions, a fuel having 40% moisture can be fired in successfully in fluidised bed with upto 150% excess air. However, due to heat losses it is not achievable. During present study, coal-pulp blend with 38% moisture is successfully fired at excess air levels of 5.1% (bed temperature 910 °C) – 11.5% (bed temperature of 790 °C) O_2 in the flue gas.This suggests that coal-pulp blend with higher moisture contents can be fired if heat losses are minimised.

Similar results were observed by Kuprianov *et al* (2006) by co-firing rice husk and sugar cane bagasse. They found that temperatures in the combustor were lowered with increase in mass fraction of sugar cane bagasse due to increase in moisture. With 55% mass fraction of sugar cane bagasse in the blended fuel they found that the temperatures were lower, but stable, than with lower sugar cane bagasse mass fraction blends. Kaewklum *et al.* (2007) also observed that moisture content of fuel has an effect on the temperature profile in the combustor andfor a particular excess air, temperatures observed to be reduced by 130 – 150°C at all locations along the combustor height when moisture content of the rice husk was increased from 11 to 35.5%. During present study, at a fixed excess air level, bed temperature for 50/50 coal-pulp blend is found to be around 100 °C lower than coal only firing.

5.6.3 The Effect of Moisture on Combustion Stability:

As it is mentioned earlier that 40/60 coal-pulp could not be successfully burned due to increase in moisture to a level at which the heat of combustion was not enough to evaporate the moisture and maintain the bed temperature high enough to sustain the combustion process.Similar results were obtained by Kuprianov *et al.* (2006) who could not burn as received sugar cane bagasse on its own in fluidised bed because of its high moisture content (48.8%). Similarly Sjaak and Jaap, (2008) have shown during tests on wood fired boilers that the combustion process cannot be sustained if the moisture content of the wood is above 60% on wet basis. Suksankraisorn *et al.* (2003) were unable to burn more than 20% simulated MSW (60% moisture) by mass fraction in coal, however, they were able to burn vegetable waste up to 30% mass fraction in coal with same moisture content.

Cliffe and Patumsawad (2001) have also shown by co-firing olive waste and coal that maximum waste content which can be mixed with coal for successful firing is 20%. Above 20% waste content, bed temperature is too low to burn the blend efficiently due to effect of high moisture.Patumsawad and Cliffe, (2002) investigated that maximum moisture content of MSW that could be burnt in their 10kW fluidised bed combustor was 20%.

Kaewklum *et al.* (2007) observed that it was not possible to burn rice husk with a moisture content of 40.2% due to instability and combustion disruption. They concluded that moisture content of 35% was a critical value for sustainable combustion of rice husk. This shows that rice husk of higher moisture content can be burned in fluidised bed as compared to MSW which can be attributed to different combustion characteristics of different fuels. Moreover, in the present study 50% pressed pulp blend with coal was successfully combusted with coal even though its moisture content was considerably higher (38%) than the MSW(20%) used by Patumsawad and Cliffe (2002) and also little bit higher than the critical value of 35% stated by Kaewklum *et al.* (2007) for rice husk.

The same authors (2002) found that at above 20% moisture content of MSW, bed temperature was below 600 °C and could not sustain combustion. Bed temperature for 10% moisture in a blend of MSW and vegetable waste was lower and more fluctuating (710 – 740°C) compared to that with 10% moisture MSW which was higher and stable at 750 °C.

However, it should be noted that Patumsawad and Cliffe (2002) used pure biomass but in the present study minimum 50% (wt/wt) of the fuel consisted of coal. Thus, the evidence of higher moisture fuel combustion in the present study could be due to different combustion characteristics of coal and MSW. However, operational parameters such as excess air and fluidising velocity can't be ignored and can have significant impact on the combustion behaviour of different fuels in fluidised beds. Fuels with 85% inert materials (theoretical furnace temperature of 1000 °C) including minerals and water and heating values as low as 5 MJ/kg can be burnt in fluidised bed combustors [Waters, 1975]. However some fuels such as olive oil waste cannot be burned in fluidised bed without supplying other energy [Khraisha *et al.* 1998].

Thus, the highest fraction of the secondary fuel and maximum moisture content that can be co-fired with coal in a fluidised bed depends upon type of the secondary fuel and possibly on the type of combustor used.

5.6.4 The Effect of Fuel Moisture on Efficiency:

Calorific value of fuels strongly influences the efficiency of the combustion process. An increase in the moisture content of fuel decreases its calorific value so that the calorific value of the coal-pulp blend decreases with increase in pulp proportion due to very low CV and high moisture content of the pulp. Theoretical effect of moisture content on the net calorific value of the fuel is shown in Figure 5.31 [Sjaak and Jaap, 2008] which clearly illustrates a decrease from around 18.7 MJ/kg at 0% moisture to around 6 MJ/kg at 60% moisture, representing a drop in the net calorific value of around 68%.

Therefore, it is expected that the efficiency of the combustion process will decreases as the moisture content of the fuel increases. The effect of moisture on the fluidised bed efficiency when co-firing blends of coal and pressed sugar beet pulp at different proportions broadly illustrates this despite variations in the measured data. Thus, the efficiency of 70/30 blend (67 – 93%) is lower than coal due to higher moisture content of the blend, however, the effect is less pronounced than probably expected due to dominance of coal in the blend. However, both the 50/50 and 60/40 blends show considerable difference from that of 70/30 blend, possibly due to increased pulp proportion and relatively higher moisture content and also

scatter in the measured values. It is also observed that efficiencies at BT for 60/40 (58 – 83%) and 50/50 (59 – 83%) blends are similar despite the higher moisture content of 50/50 blend again possibly due to scatter.It can also be due to lower elutriation at higher moisture content as a result of ignition delay. Kuprianov *et al.* (2010) also found that unburned carbon in fly ash was reduced from 1.8 to 1.1% when moisture content was increased from 8.4 to 25% due to greater contribution of wet oxidation of char by OH radicals and by higher residence time of char in the reactor caused by reduction in theoretical air requirement at higher moisture contents. However, as shown previously that athough theoretically air requirement per unit mass of fuel decreases with increase in moisture, it increases per unit energy. Therefore, the argument that efficiency drops due to increased residence time as a result of lower theoretical air requirement is not valid and most likely explaination is that increase in fuel moisture content delays ignition and thus burns in the bed and efficiency increases.

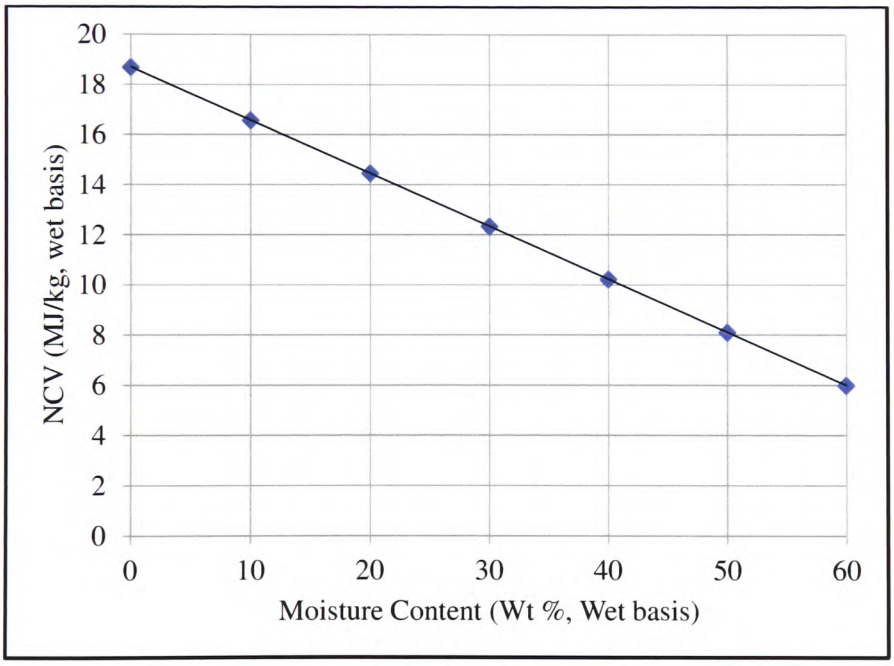


Figure 5.31: NCV as a function of fuel moisture of fuel (wet basis) with 50% C, 6% H and 44% O [Sjaak and Jaap, 2008]

Patumsawad and Cliffe, (2002) observed that with 10% moisture content blend of MSW and vegetable waste the efficiency was lower than that with 10% moisture for MSW alone and

that a moisture content of 10% in simulated MSW gave the highest combustion efficiency which decreased with increasing moisture content. They also found that carbon combustion efficiency increased from 63% with 5% moisture MSW to 70% with 10% moisture content MSW, possibly due to delay in gas evolution and increase in de-volatilisation time with increase in the moisture content of fuel [Lai and Krieger-Brockett, 1992]. Although, this phenomenon was not observed during present study and it was found that the efficiency was always lower for high moisture fuels as compared to those having relatively lower moisture. This may be due to relatively higher moisture fuels used in the present study. Nevertheless, close agreement between efficiencies for 60/40 and 50/50 coal-pulp blends supports above argument.

Patumsawad and Cliffe, (2002) also observed that at 15% moisture, blend of MSW and vegetable waste combustion efficiency was 63% and bed temperature was 650 – 700 °C compared to 15% moisture MSW which has combustion efficiency of 66% and bed temperature of 715 °C. The difference in results could be due to segregation of MSW and vegetable waste, moisture was raised by adding potatoes while in the case of MSW moisture was raised by adding water. When water is added it is uniformly absorbed by the whole mass of MSW while vegetable waste keeps its separate identity and is separated from the MSW in the combustor due to different physical properties. This may be due one of the possible reasons of data scatter in the present study as two fuels fed together keep their separate identity and burn differently.

Ash content of the fuel also has an effect on the efficiency of the combustion process. With increase in pressed pulp proportion the moisture content of the blend increases but ash content decreases, see Table 5.10, due to lower ash content of the pulp. Higher ash content fuels give lower efficiency due to increased elutriation and vice versa. Thus, higher moisture content tends to decrease efficiency and lower ash content tends to increase it. Net effect of moisture and ash could be a decrease or increase depending upon the process conditions. Although ash content does not change considerably the effect of ash on efficiency is more pronounced than moisture as demonstrated by Patumsawad and Cliffe (2002). That is possibly one of the reasons for almost similar efficiencies for the 60/40 and 50/50 blends.
Above discussion shows that the impact of co-firing on thermal efficiency can therefore be complicated although it appears to depend principally on the moisture content of the biomass

and the co-firing ratio [Battista *et al*, 1998]. At low biomass co-firing ratios and with dry biomass (moisture <10%) impacts on efficiency are modest [Sjaak and Jaap, 2008]. The effect was also observed by burning 70/30 coal-pulp blend which gave slightly lower efficiencies than coal possibly due to higher moisture content although the effect of the relatively small proportion of biomass was negligible.

5.7 Uncertainties in Efficiency:

It should be noted here that during the current combustion tests of solid fuels in the bed there is no reference made to unburned carbon going out in the fly ash. Fly ash was not measured or analysed as the flue gas was exhausted to atmosphere without passing through any gas cleaning equipment e.g. cyclone or filter. This could have an effect on the value of the efficiencies calculated.

Heat loss due to incomplete combustion primarily depends upon excess air ratio and CO concentration in the flue gas but independent of the fuel quality [Fang *et al.* 2004]. However, Kuprianov *et al.* (2010) found that heat loss due to unburned carbon is dependent on the unburned carbon content of fly ash which is influenced by the moisture content of the fuel as well as on the excess air levels.

As unburned carbon going to fly ash or remaining in the bed was not measured during the tests in this work the results do not include these energy losses. Moreover, although CO concentration in the flue gas was measured but its relatively low energy value (heat that could have been released if CO had been converted to CO_2) is not considered and is not included in the calculations. However, it is expected that there would not be a major effect on the results as all these losses are not considered in the calculations for any of the tests.

Also as mentioned earlier the variation of feed composition and flow rate is more likely to have an effect on the results. Due to the small size of the bed small variations in the feed flow can also result in significant variations in the results. Similar effects were observed by Patumsawad and Cliffe (2002) during co-firing simulated MSW of different moisture contents with coal at different excess air levels. The variation in combustion efficiency and flue gas composition was thought to be the result of non-uniform feed. When co-firing

vegetable waste with coal they could not make any conclusion on the effect of excess air on combustion efficiency due to variation in fuel feed rate. This is similar to the results for coal-pressed pulp blends where it is difficult to draw definitive conclusions concerning the reasons for the variations in behaviour of the different blends tested.

5.8 Conclusions:

On the basis of the results and discussions in this chapter the following conclusions can be drawn.

Moisture content of fuels dictates maximum proportion of the fuel which can be successfully combusted in a fluidised bed. It was not possible to burn 60% pulp blend in coal (moisture content around 45%) due to high moisture content of pulp (around 71%).

Co-firing tests with different biomass and coal blends in the fluidised bed test rig revealed that biomass has a greater tendency to burn in the freeboard. The amount of volatiles and fines which burns above the bed increases with increase in excess air level that is why the gap between the bed and freeboard temperatures found to be decreased at higher excess air levels. It is found that over the range of test conditions and the coal pulp blends tested at least 50% of the pulp burns above the bed. The bed and freeboard temperatures were found to be decreased with increase in moisture content of the fuel.

In contrast to combustion efficiency which decreases with increase in excess air, fluidised bed efficiency defined as the tendency of the fluidised bed to produce hot combustion products is found to be increased with increase in excess air due to better air fuel mixing. Despite uncertainty in the data the efficiency also found to be lower for higher moisture fuels.

Amount of excess air required to maintain a fixed bed temperature decreases with increase in fuel moisture content. For coal-pulp blends air requirement for the same bed temperature was found to be decreased by about 20%. While for coal and wood chips tests excess air decreased by 30%. This reduction in excess air will be beneficial in enhancing the throughput of the HGG at British Sugar, Cantley.

Chapter 6

Emissions from Combustion Tests

6.1 Introduction:

Combustion is a complex phenomenon that requires the right mixing, turbulence, sufficient temperature and enough time. If combustion is not properly controlled pollutants can form. Atmospheric emissions are very important when considering a combustion process. These emissions include sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon oxides (CO_x), particulates, unburned hydrocarbons etc. SO_x and NO_x are responsible for acid rain and ozone depletion while CO_2 is a greenhouse gas. Fuel properties, type of combustion system, method of combustion and operating conditions affect these emissions formation.

Emissions of SO_2, by custom, include the sum of concentration of SO_2 and SO_3. SO_3 is typically only 3 – 4% of the total sulphur oxide emissions [Oka and Anthony, 2003] and therefore is not usually considered. Emissions of NO_x include NO and NO_2 where typically NO are about 95% of the NO_x from coal combustion. Emissions of NO_x do not take N_2O into account as it is considered separately.

The European Union (EU) has recently upgraded emissions standards for combustion plants in EU directive titled "Directive 2010/75/EU of the European Parliment and of the Council of 24 November 2010" on industrial emissions (integrated pollution prevention and control). The directive states that all emission limit values shall be calculated after correction for the water vapour content of the waste gases and at a standardized O_2 content of 6% for solid fuels, 3% for combustion plants other than gas turbines and engines using liquid and gaseous fuels and 15% for gas turbines and gas engines. Emission limits set by EU for SO_2 and NO_x are given in Tables 6.1 and 6.2, respectively.

Emissions of NO_x, SO_x and CO measured during the tests are presented in this chapter. The effect of operating conditions and fuel characteristics on the emissions of these pollutants is

discussed. Formation and destruction mechanisms of these pollutants are also presented. The results are discussed in relation to data available in open literature.

Table 6.1: Emission Limit Values (mg/Nm^3) for SO_2 for combustion plants using solid or liquid fuels with the exception of gas turbine and gas engines [EU Directive, 2010/75/EU]

Total rated thermal input (MW)	Coal, lignite and other solid fuels	Biomass	Peat	Liquid fuels
50 – 100	400	200	300	350
100 – 300	250	200	300	250
>300	200	200	200	200

Table 6.2: Emission limit values (mg/Nm^3) for NO_x for combustion plants using solid or liquid fuels with the exception of gas turbine and gas engines [EU Directive, 2010/75/EU]

Total rated thermal input (MW)	Coal, lignite and other solid fuels	Biomass and Peat	Liquid fuels
50 – 100	300 450[1]	300	450
100 – 300	200	250	200 450[2]
>300	200	200	150 450[2]

[1]In the case of pulverized lignite combustion

[2]For firing crude residues

6.2 Emissions from Natural Gas:

Emissions of NO_x (g/kW and mg/Nm^3), corrected to 3% O_2, from the tests with natural gas have been plotted in Figure 6.1 as a function of power input at different excess air levels. As can be seen from the figure that the data is very much scattered and no clear conclusion can be made. The possible reason for this could be the mix of combustion and dilution

(secondary) air. As staged combustion is a technique used to reduce NO_x emissions, the dilution air might have a staging effect on the NO_x emission levels to give lower values. As split between the combustion and dilution air is not measured separately for a particular test, it is not possible to comment on the effect of air staging on the results.

Ultimate analysis of natural gas shows that it contains no sulphur thus no SO_2 emissions were observed during the tests with natural gas.

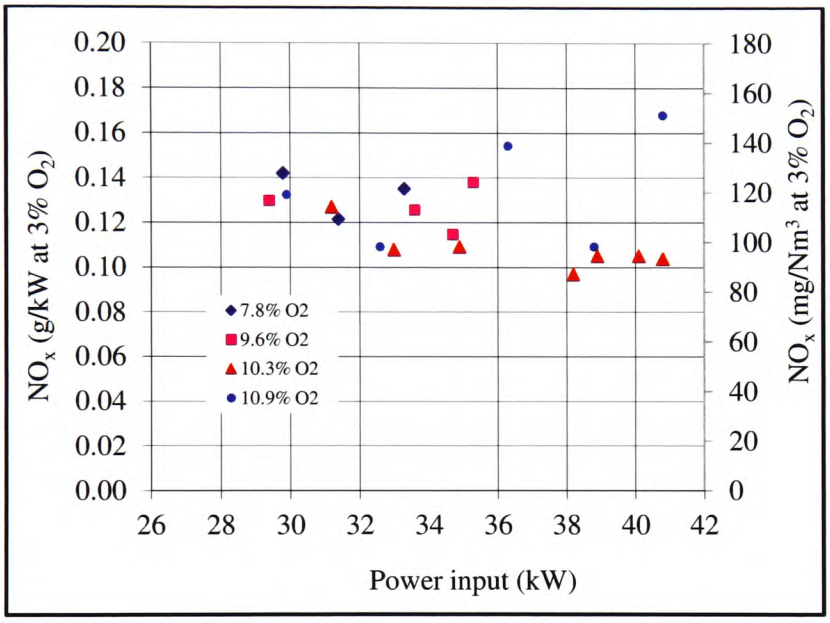


Figure 6.1: NO_x as a function of power input at different excess air levels

6.3 Emissions from emulsion tests:

The effect of high moisture biomass on the bed behaviour and emissions is investigated during gas oil and emulsion (gas oil + water) firing in the bed. Emissions data is taken at different power inputs and excess air levels.

It is noted that by introducing gas oil into the bed at a flow rate of 0.9 l/hr (10kW), when the rig is fired with natural gas at 37 kW and 11.8% O_2 in the flue gas to get a stable bed

temperature of 798 °C, NO_x levels slightly increased from 20 to 33 ppm and SO_2 varied between 100 and 300 ppm while CO varied from 900 to 2400 ppm. Emissions of SO_2 are due to the presence of 0.9% sulphur in gas oil and those of CO are possibly due to incomplete combustion.

Emissions of NO_x during tests with oil-water emulsions varied from 27 – 40 ppm (corrected to6% O_2) for 50/50 and from 41 to 58 ppm (corrected to 6% O_2) for 30/70 emulsion. Similarly the emissions of SO_2 varied from 60 to 193 ppm (corrected to 6% O_2) for 50/50 emulsion and from 8 to 32 ppm (corrected to 6% O_2) for 30/70 emulsion. Detailed study of this topic is beyond the scope of this thesis as tests with gas oil and its emulsions with water are carried out to understand the fluidised bed behaviour and its responses to liquid and high moisture fuels.

6.4 Emissions from Thoresby coal:

The measured NO_x emissions (normalised to 6% oxygen) for a range of fluidised bed operating conditions for Thoresby coal are presented in Figure 6.2 and compared with calculated values using a correlation from BCURA Manual (2005) for large scale plants. The correlation predicts NO_x emissions at different bed temperature, oxygen content of the flue gas and over-fire air levels. As over-fire air is not used in the present study, the correlation is modified and the over-fire term is omitted. The resultant correlation is;

$$NO_x \text{ (mg/m}^3 \text{ at 6\% } O_2 \text{ volume dry at 273 °K)} = -853.6 + (1.1133*T) + (93.05*O_2)$$

The correlation predicts that a reduction of 100mg/Nm^3 in NO_x emissions can be achieved by reducing bed temperature by 100 °C or by reducing the O_2 in flue gas by 1%. However reduction is NO_x emissions cost in terms of drop in combustion efficiency. For example, if a fluidised bed is fired with a coal having a nitrogen content of 1.33% at a bed temperature of 850 °C at 4% O_2 in the flue gas giving 91% combustion efficiency, predicted NO_x emissions are 465 mg/m^3 which equates to a 10% conversion of fuel nitrogen. However, when the bed temperature is increased to 900 °C and O_2 in flue gas to 6%, NO_x emissions increase to 710 mg/m^3 (15.3% conversion of fuel nitrogen) with an increase in combustion efficiency to 96.5%.

The figure shows a close agreement between the measured and predicted values calculated from the correlation keeping in mind that nitrogen content of the Thoresby coal (1.62%) is higher than the coal used to develop the correlation (1.33%). Moreover, in a survey of measured data for different sized fluidised beds, Gulyurtlu (1995) found that NO_x emissions appeared to be greater on pilot scale facilities than on much larger plants. He did not explain the reason but it could be possibly due to better control of operating conditions at commercial facilities. Consequently the relatively high levels measured in the current tests are not "out of line" with those observed in other studies. The emissions of NO_x measured during the tests correspond to a variation of fuel nitrogen conversion of about 24 – 32% over the experimental conditions tested with an average of 28% (converted to 6% O_2) based on the 1.62% nitrogen in Thoresby coal. BCURA manual (2005) reported variation of NO_x emissions from 600 mg/m^3 to 1500 mg/m^3 (6% O_2 dry) with fuel nitrogen conversion factor variation from 17 to 33% with most of the results close to 23% fuel nitrogen conversion which are not far from the measured values. The figure also shows the effect of bed temperature on NO_x emissions at different operating conditions. It can be seen from the figure that the emissions are not very much affected by temperature and tended to increase only slightly with bed temperature which suggests that thermal NO_x makes a very small contribution as would be expected at these bed temperatures, so that fuel NO_x is the dominant NO_x formation mechanism.

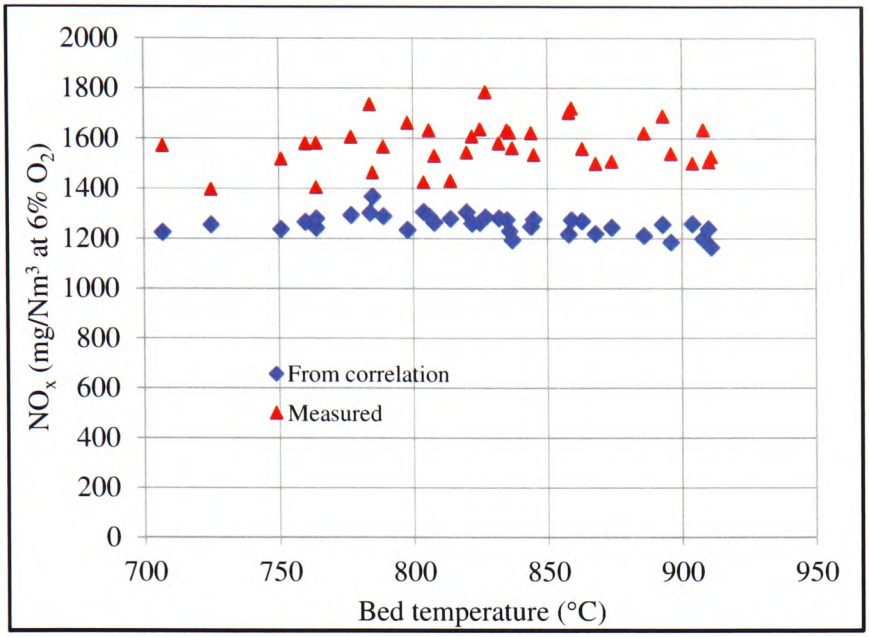


Figure 6.2: Comparison of the measured and Predicted NO_x Emissions from coal

Sulphur dioxide emissions (averaged and normalised to 6% O_2) are plotted as a function of bed temperature in Figure 6.3. The figure shows that SO_2 emissions increase with increases in bed temperature. The measured values correspond to about 60 – 66% conversion of fuel sulphur into SO_2 calculated on the basis of 2.01% sulphur content in the coal [BCURA, 2006] and 80 – 88% sulphur conversion on the basis of 1.5% sulphur in coal [British sugar]. These conversion efficiencies are reasonable taking into account sulphur trapped in the ash, the formation of SO_3 and uncertainties in the composition of coal. Also during the present work coal and biomass were fed above the bed and most of the volatiles could have been evolved in the freeboard region. In this case sulphur retention is reduced due to a lower contact with the bed material and ash. Thus SO_2 emissions measured could have been different if feed had introduced into the bed instead of on the bed.

Emissions of CO normalised to 6% O_2 from Thoresby coal as a function of excess air (O_2 %) at different thermal inputs are plotted in Figure 6.4. The CO emissions are plotted against O_2 as they are affected mainly by excess air. Although the data is scattered, the figure shows that CO emissions increase with increase in thermal input at a particular excess air level. A close look at the figure reveals that for a particular thermal input the emissions first decrease with

increasing excess air and then increase as excess air is further increased. Thus there is an optimum excess air at which CO emissions are at minimum, seems to be at around 12 – 12.5% O_2 in the flue gas.

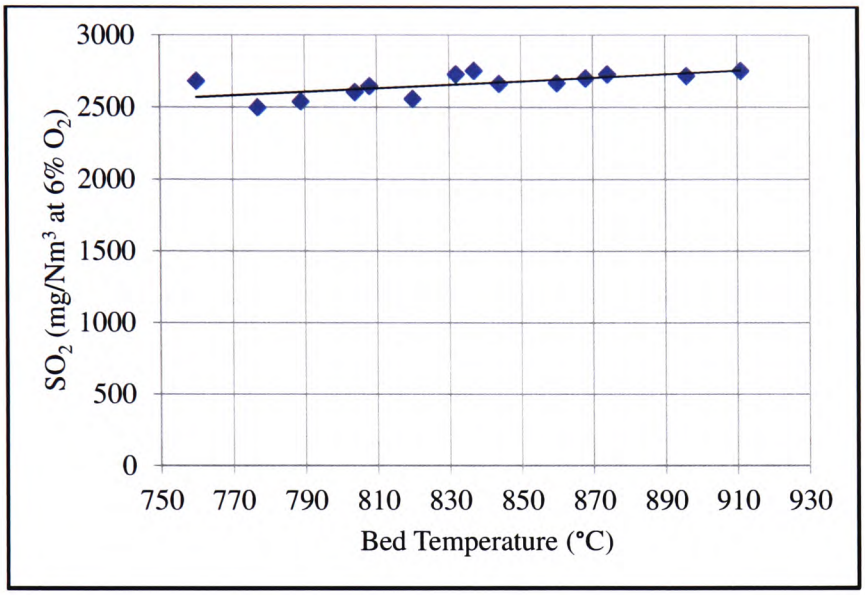


Figure 6.3: Bed temperature Vs. Sulphur Dioxide Emissions from Thoresby coal

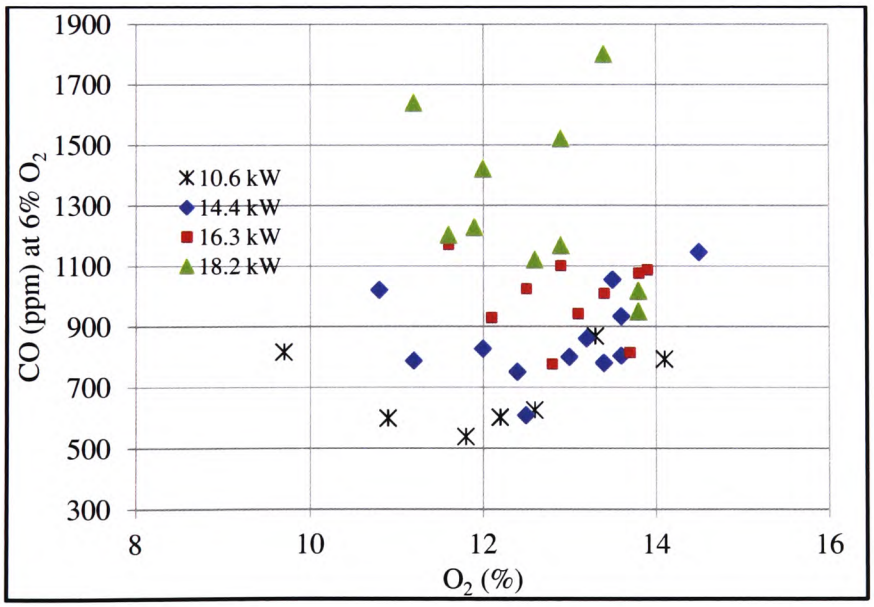


Figure 6.4: CO emissions from Thoresby coal

6.5 Emissions from Co-Firing Wood Pellets and Coal:

Nominally the wood pellets have very low nitrogen and sulphur contents so that lower emissions of NO_x are achieved when burning not only the pellets as a single fuel but also with the 50/50 coal-pellets blend, see Figure 6.5. The figure shows NO_x emissions in mg/Nm^3 corrected to 6% O_2 in the flue gas as a function of bed temperature. As can be seen from the figure that the data is scattered but it is clear than NO_x emissions with wood pellets and Thoresby coal are in the range of 200 – 400 mg/Nm^3 and 1600 – 1800 mg/Nm^3, respectively. This shows that emissions of NO_x for wood pellets are almost 4.5 – 8 times lower than those from the coal. The figure also shows NO_x emissions for 50/50 coal/pellets blend, most of which are in the range of 600 – 800 mg/Nm^3 almost half of those from coal and almost 2.3 times those from pellets.

Blend of 50/50 coal and pellets shows intermediate behaviour but emissions from the blend are lower than expected on the basis of emissions data from the combustion of individual fuels although nitrogen content of the blend (0.85%) is almost half of that of coal (1.62%). This could be due to the tendency of biomass to reduce NO_x emissions. It is believed that during co-firing, combustion of biomass reduces NO_x emissions as most of the fuel bound nitrogen in biomass is converted to ammonia during combustion process. This ammonia reacts with already formed NO to produce molecular nitrogen thus provide an in situ source of $DeNO_x$. This is one of the possible ways biomass can contribute to lower NO_x emissions. Rest of the mechanisms for NO_x reduction and effect of operating parameters on NO_x formation and destruction are discussed later in this chapter.

Similar results were obtained for the emissions of sulphur dioxide. Emissions of SO_2 for coal, pellets and 50/50 coal-pellets blend are plotted in Figure 6.6 as a function of bed temperature. It can be seen from the figure that SO_2 emissions from the combustion of 50/50 coal-pellets blend and pellets alone are almost 2.5 times and 10 times lower than those from coal only combustion, respectively. The figure shows that SO_2 emissions, in all the cases show similar trend and slightly increase with increase in bed temperature.

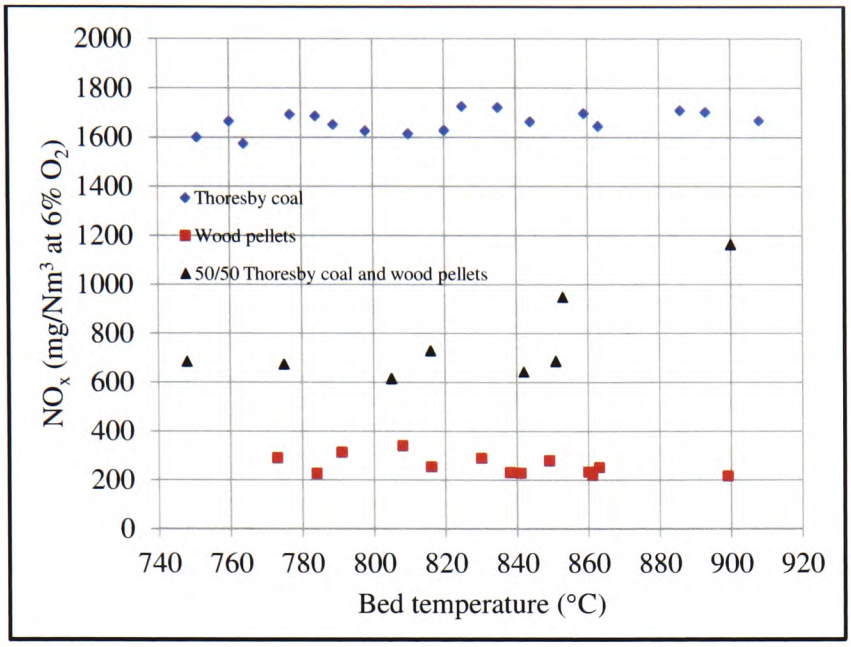


Figure 6.5: Comparison of NO_x Emissions for Coal, Pellets and their 50/50 blend

Sulphur content of the blend is (1.01%) almost half of that of coal (2.01%) due to negligible sulphur in pellets (0.01%). On the basis of fuel sulphur content SO_2 emissions from the blend should have been half of those from coal. However, it can be seen from the figure 6.6 that emissions of SO_2 show similar behaviour as shown by NO_x emissions i.e. with 50/50 blend emissions are lower than the average value expected on the basis of coal and pellets alone firing. This can be attributed to the tendency of biomass to reduce SO_2 emissions and sulphur retention by biomass ash. Mechanisms for the formation and reduction of SO_2 and the effect of operating parameters on SO_2 emissions will be discussed later in this chapter.

Emissions of CO (ppm) corrected to 6% O_2 from the combustion of pellets and their 50/50 blend with coal arepresented in Figure 6.7. The data is plotted as a function of excess air for almost similar thermal inputs from the fuels tested. Although the data is scattered, it can be seen from the figure that the emissions are generally higherfor pellets than for coal (Figure 6.4) and 50/50 blend shows an intermediate behaviour. Again, it can be observed from the figure that CO emissions seem to be the lowest at 12 – 12.5% O_2 in the flue gas.

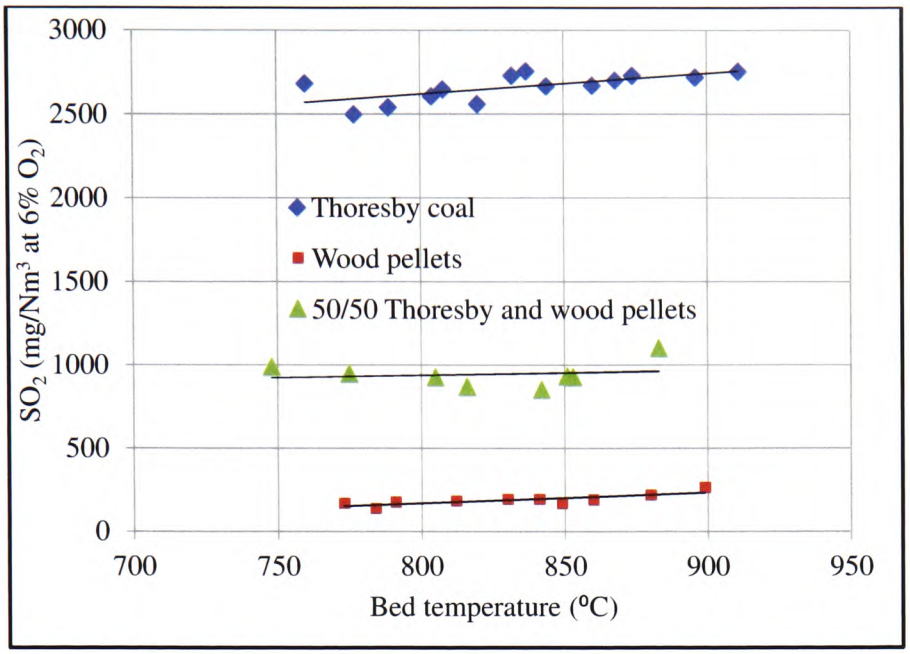


Figure 6.6: Comparison of SO_2 emissions from coal, pellets and their blend

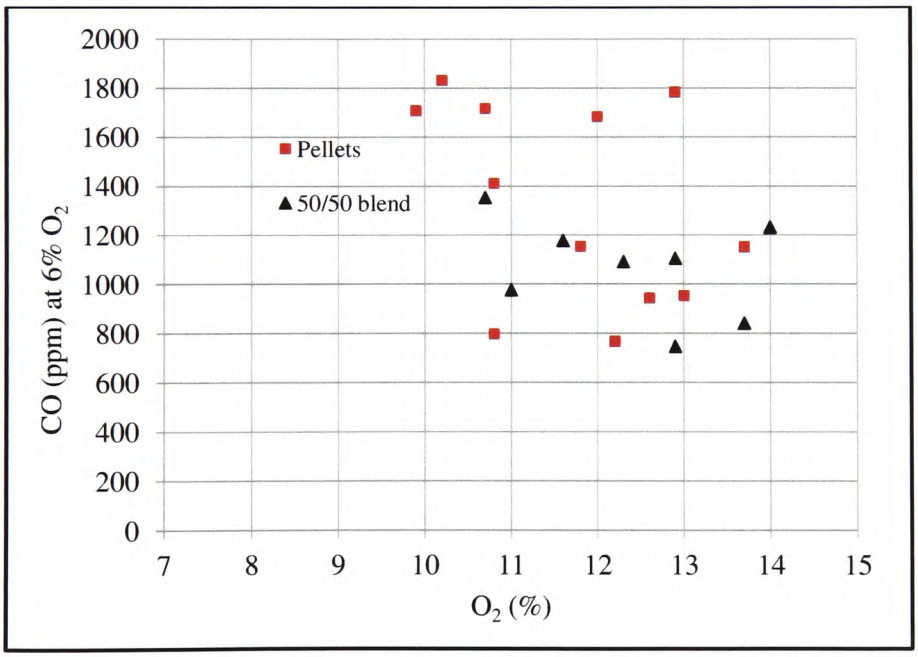


Figure 6.7: CO emissions from pellets and 50/50 blend with coal

6.6 Emissions from Co-Firing Wood Chips and Coal:

As received wood chips (15% moisture) and those soaked in water (to attain moisture content of 55%) are co-fired with Thoresby coal. It is thought that an increase in moisture content of fuel reduces NO_x emissions. Figure 6.8 which is a plot of NO_x emissions (normalised to 6% oxygen) against bed temperature shows that there is relatively little difference in the NO_x emissions in the two cases (15%M and 55%M blends). The levels of 600 – 700 mg/Nm^3 are very similar to those observed in most of the tests with a 50/50 blend of coal and wood pellets.

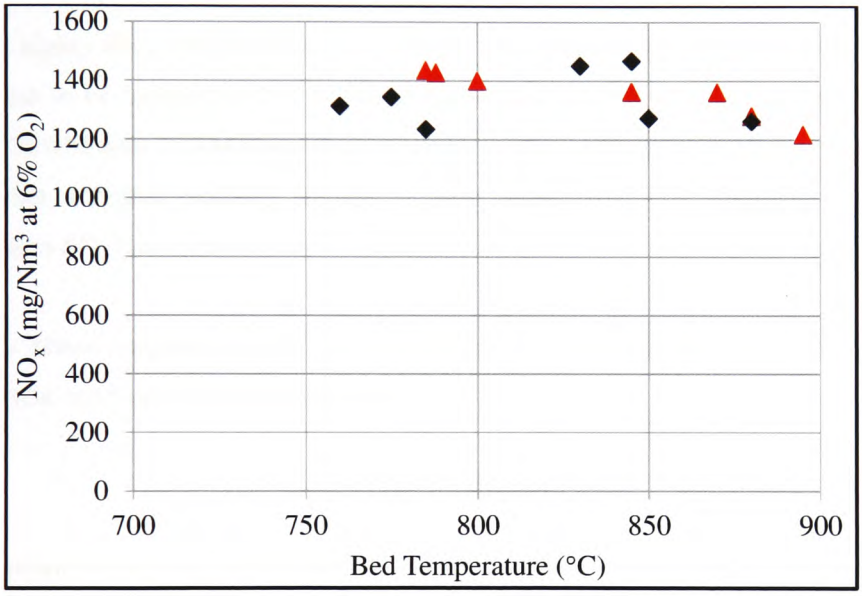


Figure 6.8: NO_x Emissions when Co-Firing Coal and Wood Chips

Kouprianov and permachart (2003) have shown that, by firing woody sawdust in a conical fluidised bed combustor with a conical bottom having 20 degree angle and 1m height and cylindrical top with 0.9m diameter and 2m height, NO_x emissions were reduced with increased moisture content in fuel but this was accompanied by an increase in CO emissions. However, results obtained during the present study with woody biomass show very little influence of moisture content on NO_x if compared to those observed by Kouprianov and permachart (2003). The results suggest that blends of wood chips and pellets with coal show similar NO_x emissions regardless of their moisture content. Thus the effect of moisture on

NO_xemissions is negligible. One possible reason could be that the mass contribution of the higher moisture wood chips in the blend is lower and thus less volatiles are introduced into the bed. This reduction in volatiles reduces the NO_x reduction tendency and the net effect of higher moisture and lower volatiles is balanced.

Emissions of SO_2 as a function of bed temperature for 15%M and 55%M blends are plotted in Figure 6.9. The figure shows that SO_2 emissions increase with increase in bed temperature and thus decrease with increase in excess air. Comparison of the results shows that SO_2 emissions for 55%M are around 30% lower than 15%M blend. Dry mass contribution of coal is higher in 55%M blend than in 15%M blend. On dry basis sulphur content of 55%M blend (1.43%) is higher than 15%M blend (1.11%). On the basis of sulphur content the emissions are expected to be higher for 55%M blend than 15%M blend but due to higher moisture content of 55%M than 15%M blend the emissions are lower for the former. A possible reason could be that at higher moisture content of fuel, higher the water vapour in the flue gas, which reduces SO_2 emissions by converting SO_2 to H_2SO_4 by the following reactions.

In the gas phase sulphur dioxide is oxidised by reaction with hydroxyl radical via an intermolecular reaction [Weathers and Likens, 2007].

$$SO_2 + OH^{\cdot} \rightarrow HOSO_2^{\cdot} \qquad (6.1)$$

As O_2 is present in the flue gas the $HOSO_2\cdot$ could have been reacted by the following reaction to form sulphur trioxide:

$$HOSO_2^{\cdot} + O_2 \rightarrow HO_2^{\cdot} + SO_3 \qquad (6.2)$$

In the presence of water, sulphur trioxide (SO_3) is converted rapidly to sulphuric acid by the following reaction:

$$SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4 \qquad (6.3)$$

As the moisture content of fuel increases, more OH radicals are produced and thus potential of conversion of SO_2 to H_2SO_4 via the above reactions increases. This is possibly the reason for the lower SO_2 emissions for 55%M blend.

Emissions of CO, normalised to 6% O_2, for coal and chips blends are plotted in Figure 6.10 as a function of excess air. The figure also compares the emissions with those from coal-pellets blend. Although the data is scattered, it can be seen from the figure that the emissions for 15%M blend are considerably higher than those for pellets blend possibly due to comparatively difficult combustion of wood chips than pellets as pellets are a prepared biomass and relatively easy to burn thus produce low CO emissions. The emissions for 55%M are lower than those for 15%M possibly due to delayed and slow evolution of volatiles with increase in fuel moisture.

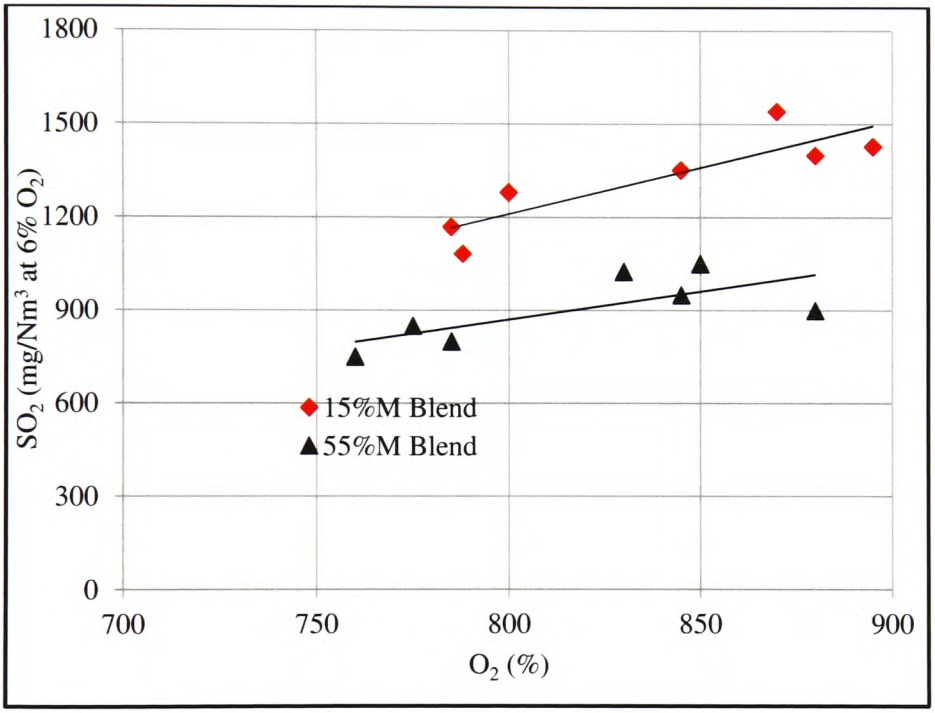


Figure 6.9: SO_2 Vs. O_2 for Coal-Chips blends

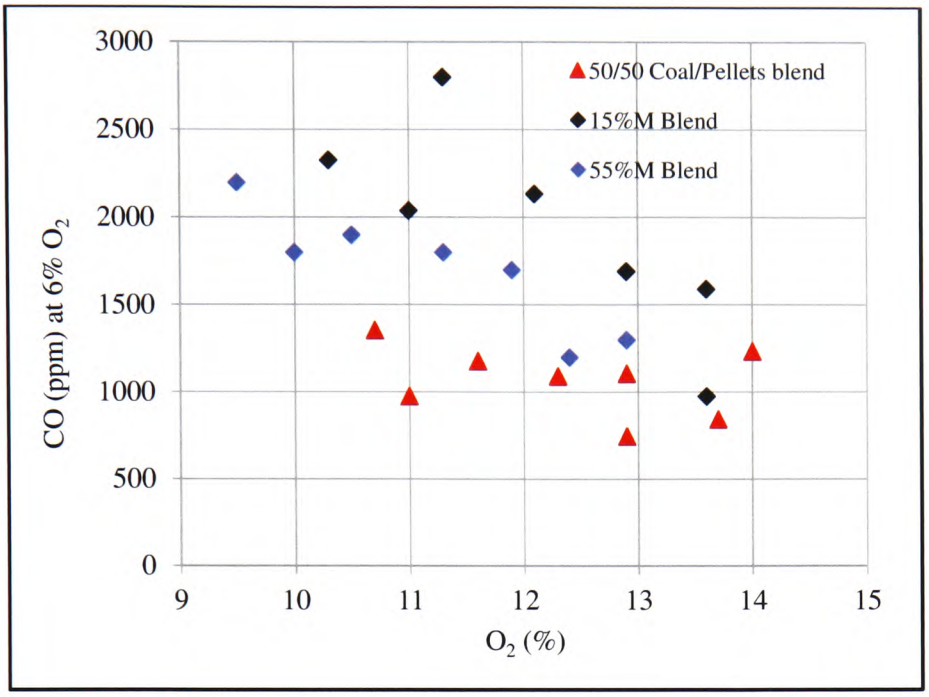


Figure 6.10: CO Emissions for Coal-Chips blends compared with Coal-Pellets blend

6.7 Emissions from Co-Firing Pulp and Coal:

Emissions data for NO_x and SO_2 for coal-pulp blends is summarised in Table 6.3. The normalised NO_x emissions at 6% O_2 for coal-pulp blends are compared with those for coal alone in Figure 6.11. NO_x emissions for blends are only 12 – 22% lower than those for coal although "as received" nitrogen content of pulp (0.14%) is considerably lower as compared to 1.62% for the coal. However, the dry matter contribution of pulp in the blends is very low as compared to coal. Thus coal nitrogen plays a dominant role in the formation of NO_x due to its higher mass contribution. Nitrogen conversion for the blends is between 26% and 32% which is almost the same as that for coal as mentioned previously. As emissions of NO_x for blends are lower than coal a further benefit of co-firing pressed pulp should be a reduction in NO_x on the full-sized plant at British Sugar.

Table 6.3: Emissions comparison from Coal and Coal-PP blends

	NO_x (mg/Nm^3 at 6% O_2)	SO_2 (mg/Nm^3 at 6% O_2)
Thoresby coal	1600 – 1800	2500 – 2750
70/30 blend	1200 – 1600	1600 – 2400
60/40 blend	1200 – 1500	1000 – 1500
50/50 blend	1200 – 1500	500 – 1000

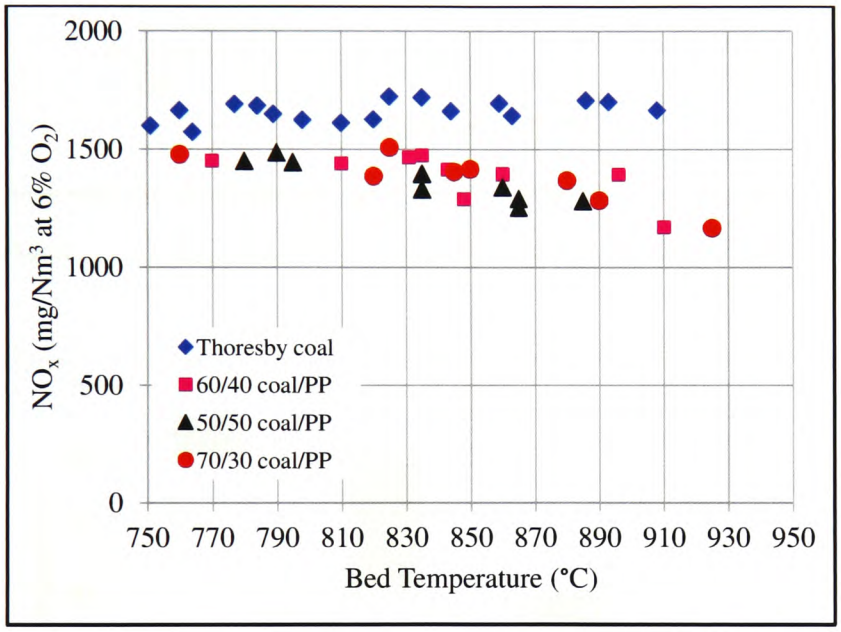


Figure 6.11: Comparison of NO_x emissions from coal and 50/50 coal-PP blend

Emissions of SO_2 in mg/Nm^3 corrected to 6% O_2 for coal and coal-pressed pulp blends are shown in Figure 6.12. The figure shows that SO_2 emissions for blends are lower than those for coal. Although the data is scattered nevertheless it is clear that the emissions decrease with increase in proportion of pressed pulp in blend. Based on the sulphur content of the blends given in Table 6.4, most of the data corresponds to a sulphur conversion of 40% – 60%, 26% – 40% and 14% – 27% for 70/30, 60/40 and 50/50 coal-PP blends, respectively, see Figure 6.13.

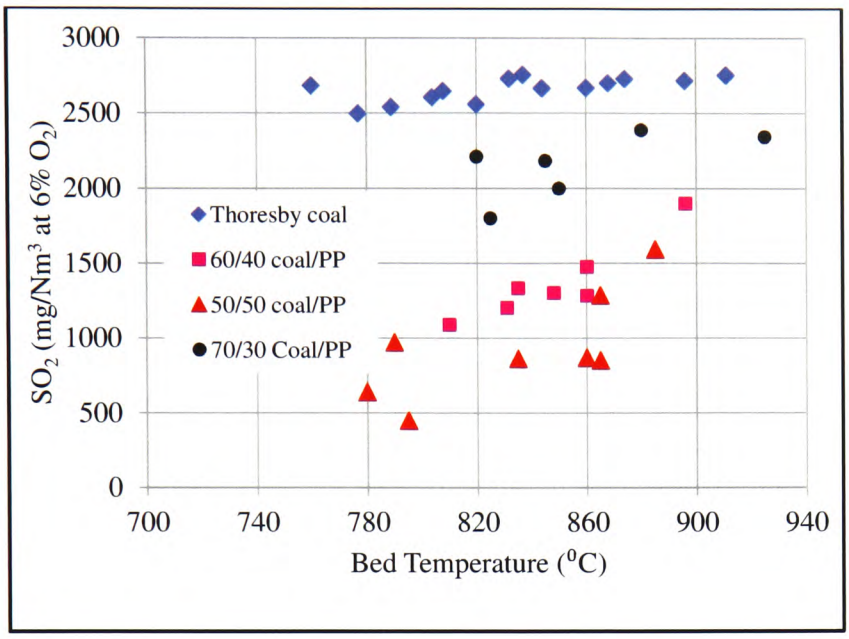


Figure 6.12: Comparison of SO_2 emissions from coal and coal-PP blends

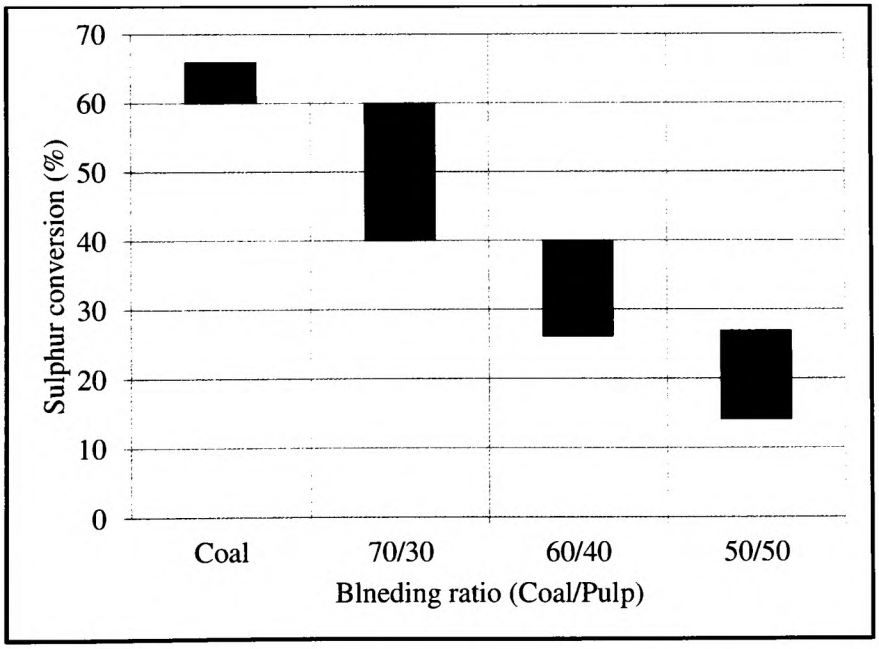


Figure 6.13: Sulphur conversion for coal and coal-PP blends

The lower conversion with increased proportion of pressed pulp is also possibly due to the increase in moisture which absorbs SO_2. With increasing pulp proportion, moisture content of the blend increases and thus more OH radical are available to convert produced SO_2 to H_2SO_4 by the reactions mentioned in Section 6.6. Also retention of sulphur by biomass ash could be another possibility. The figure 6.12 also shows that the emissions increase with increasing bed temperature. The effect of bed temperature on SO_2 emissions seems to be more pronounced at higher pulp proportions in the blends.

The maximum SO_2 capture by CaO is achieved at Ca/S molar ratio between 2.5 and 4 [Nowak, 2003]. As the Ca/S ratio for all the fuels and fuel blends tests is very much lower than this optimum requirement, see Tables 6.4 and 6.8, that is why the conversion of sulphur to SO_2 is relatively higher (14 – 60% for coal-pulp blends).

Savolainen (2003) also observed slightly higher SO_2 emissions with coal than with co-combustion of sawdust and coal due to higher S content of coal than wood. Sulphur forms gaseous compounds SO_2, and SO_3, and alkali sulphates during the combustion process. About 40% – 90% of total sulphur in the biomass fuel is bound in the ash and the remainder is carried in the flue gas as SO_2 and to a minor extent as SO_3. Thus SO_2 emissions are lower when blending biomass with coal.

Comparison of results shows that SO_2 emissions for 15%M are similar to 60/40 coal-pulp blend despite lower sulphur content of the former. This is possibly due to the higher moisture content of the 60/40 blend (31.8%) as compared to 15%M (10%) which may have reduced SO_2 emissions by converting it to H_2SO_4. Thus the net effect of higher sulphur and higher moisture content in this case seems to be almost balanced. The emissions from 55%M blend are lower than 60/40 blend although the moisture content of 55%M blend is similar to 60/40 coal-pulp blend. This could be due to lower sulphur content of 55%M blend than 60/40 coal-pulp blend. Another possible reason could be higher (32.2%) dry biomass contribution in the case of 55%M blend as compared to 60/40 coal-pulp blend which contains only 17% biomass on dry basis. Higher proportion of biomass during co-firing results in lower SO_2 emissions due to sulphur retention by biomass ash.

Table 6.4: Nitrogen and Sulphur contents of Coal and Coal-PP blends

	50/50	60/40	70/30	100/0
Nitrogen, AR (%)	0.88	1	1.2	
Nitrogen, Dry (%)	1.42	1.50	1.57	
Nitrogen, DAF (%)	1.51	1.59	1.66	
Sulphur, AR (%)	1.08	1.26	1.45	2.01
Sulphur, Dry (%)	1.74	1.85	1.93	
Sulphur, DAF (%)	1.84	1.95	2.04	
Ca, AR (%)	0.66	0.55	0.44	0.12
K, AR (%)	0.41	0.34	0.27	
Na, AR (%)	0.16	0.17	0.18	
Fe, AR (%)	0.45	0.54	0.63	
Ca/S (Mass)	0.61	0.44	0.31	0.06
Ca/S (Molar)	0.49	0.35	0.25	0.05
Moisture (%)	38.3	31.76	25.22	

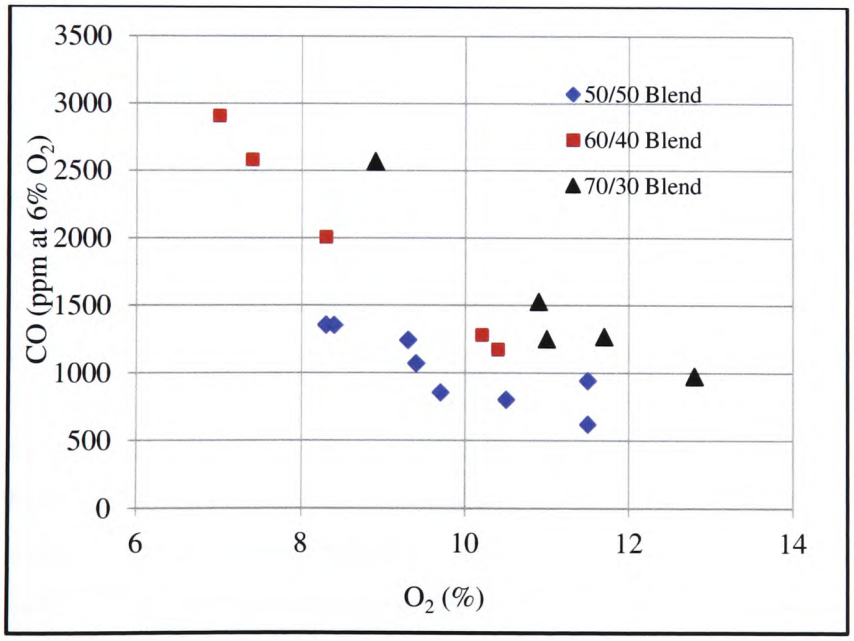


Figure 6.14: Carbon monoxide emissions from coal-PP blends

Emissions of CO normalised to 6% O_2 for coal and pressed pulp blends against O_2 concentration in the flue gas (excess air) are plotted in Figure 6.14. The figure shows that CO emissions are the highest for 70/30 blend and decrease with increase in pressed pulp proportion in the blend possibly due to delayed evolution of volatiles as a result of increased moisture content with increasing pulp proportion in the blend. The figure also shows that the emissions decrease with increase in excess air.

6.8 Effect of operating conditions and Fuel Characteristics on Emissions:

So far in this chapter NO_x, SO_2 and CO emissions data for tests conducted with different fuels at a wide range of operating conditions is presented. Following paragraphs discuss the effect of fuel characteristics and operating conditions on the emissions.

6.8.1 NO_x Emissions:

Emissions of NO_x normalised to 6% O_2 for different fuels tested are summarised in Table 6.5. The emissions for all the solid fuels and combinations of fuels are considerably higher than limits set out by EU Directive [EU Directive, 2010/75/EU], see Table 6.2. However, because of the research nature of the project, no control measures have been adapted as are used in the industry on full scale plants.

The data shows that the emissions are the highest for coal and the lowest for wood pellets. The emissions for wood pellets and 50/50 coal-pellets blend are considerably lower than coal-wood chips blends. This is possibly due to higher nitrogen content of chips (0.95%) than pellets (0.08%). It is interesting to note that the emissions for 15%M and 55%M are similar although proportion of coal in the 55%M blend on dry basis is higher. However, the emissions for different coal-PP blends are relatively higher than coal-pellets blend due to very low proportion of combustible matter contributed by pressed pulp in the blends. Due to higher proportion of coal dry matter, nitrogen content of coal-pulp blends varies between 0.9 and 1.2 which is in the same range as coal-chips blends (1.1 and 1.3%). That is why the emissions of NO_x for coal-pulp and coal-chips blends are similar. The mechanisms of NO_x formation and destruction during combustion and the effect of different parameters on NO_x emissions are described as follows.

Nitrogen in fuel is the greatest source of NO_x and N_2O during fluidised bed combustion. The conversion of coal nitrogen to NO_x and N_2O ranges from 10% [Braun, 1990] to 30% [Suzuki *et al.* 1991] depending upon the type of coal. Only a small percentage of NO_x produced come from atmospheric nitrogen (thermal and prompt) at typical fluidised bed temperature of 800 – 900 °C [Halgaard, 1991]. Fuel NO_x formation takes place by the combustion of nitrogen containing species released during volatilisation and oxidation of nitrogen retained in char. Fuel NO_x are very sensitive to stoichiometric conditions. Prompt NO_x, contributes the minimum to the total NO_x, and results from radicals of hydrocarbons reacting with atmospheric nitrogen. These reactions give NH_3 and HCN under fuel rich conditions. These NH_3 and HCN are oxidized to NO in lean zone of the flame [Mahmoudi *et al.* 2010].

Table 6.5: Emissions of NO_x from different fuels tested

Fuel	NO_x (mg/Nm^3 at 6% O_2)
Natural gas	90 – 130*
Coal	1600 – 1800
Pellets	200 – 400
Coal-Pellets blend (50/50)	600 – 800
Coal-15% moisture Chips blend (50/50)	1200 – 1500
Coal-55% moisture Chips blend (50/50)	1200 – 1500
Coal-Pressed Pulp blend (50/50)	1200 – 1500
Coal-Pressed Pulp blend (60/40)	1200 – 1500
Coal-Pressed pPlp blend (70/30)	1200 – 1600

*Emissions for natural gas are normalised to 3% O_2

Different pathways for the conversion of nitrogen during coal combustion are summarised in Figure 6.15. There are more than 80 possible reaction mechanisms for N_2O and NO_x formation in fluidised bed combustion. There are over 90 reactions of HCN which play a key role in the formation of NO_x and N_2O from the nitrogen released during de-volatilisation [Halgaard, 1991; Gustavsson and Leckner, 1990; Johnsson *et al.* 1990; Johnsson, 1990]. Most of the NO, N_2O, NH_3 and HCN is formed during de-volatilisation stage although de-volatilisation step is much shorter than char combustion. NO is also formed in significant

amounts during char combustion, however N_2O, NH_3 and HCN are not considered important [Winter, *et al.* 1999].

When a fuel particle is heated up, NH_3 and HCN are released and oxidised in complex reaction mechanisms with O and OH to form NO [Kilpinen and Hupa 1991]. NH_3 is oxidized to NO by the following reaction [Kilpinen and Hupa, 1991].

$$NH_3 + 5/4O_2 \rightarrow NO + 3/2H_2O \quad (6.4)$$

N_2O is not observed as it is thought to be destroyed in the flame mainly by the following reaction and is converted to molecular nitrogen [Winter, 1997].

$$N_2O + H \rightarrow N_2 + OH \quad (6.5)$$

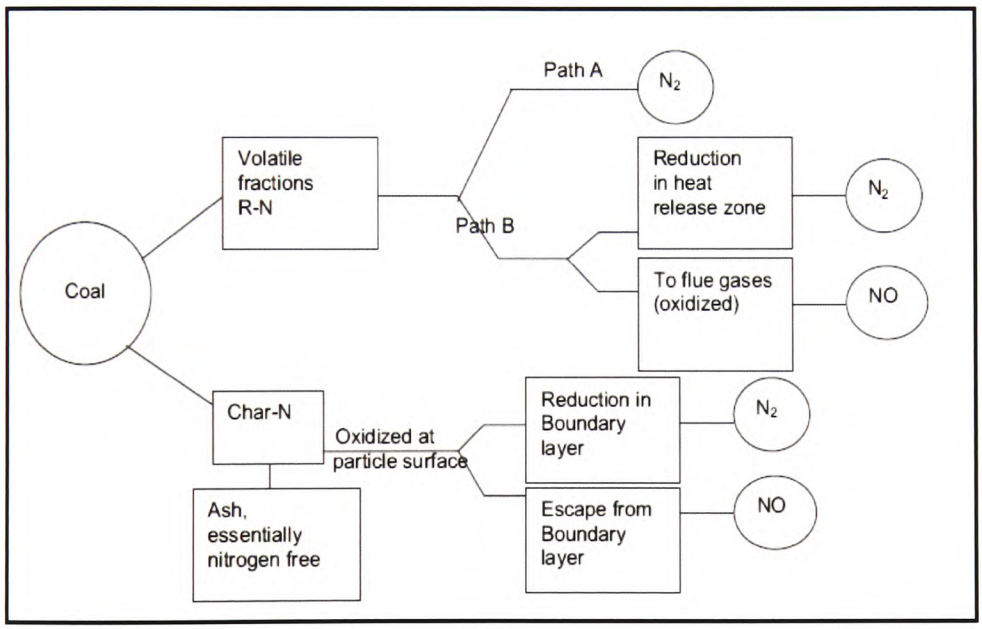


Figure 6.15: Fate of Coal Nitrogen during Combustion [Heap and Folsom, 1976]

Formation of HCN and NH_3 also depends upon heating rate. Bassilakis *et al.* (1993) found that at lower heating rates volatile nitrogen product is NH_3 while at higher heating rates the product is HCN. HCN is evolved primarily from the fuel while NH_3 evolves from the fuel in

small amounts as well as produced mainly from the conversion of HCN by reaction (6.6) with H.

$$HCN + 2H \rightarrow NH_3 + C \quad (6.6)$$

Formation of fuel rich zone adjacent to the fuel particle effectively reduces NO. Higher de-volatilisation rate leads to fuel rich zones close to fuel particles and results in NO reduction [Winter *et al.* 1999]. HCN is the main precursor to N_2O. It oxidizes to NCO by O and OH radicals which is converted to N_2O and CO by reacting with NO by the following reaction (6.7) [Winter *et al.* 1999]. In the presence of moisture rate of production of NCO can increase due to the production of more OH radicals and thus conversion of NO to N_2O by reaction 6.7 can increase which can result in lower NO_x emissions.

$$NCO + NO \rightarrow N_2O + CO \quad (6.7)$$

Volatile nitrogen is predominantly converted to NO but conversion levels are different for different fuels. Fuels, having higher nitrogen content, show lower nitrogen conversion as compared to those with lower nitrogen content. NH_3 can convert to NO and also can act as a reducing agent. That is why it is used in thermal $DeNO_x$ and Selective Non-Catalytic Reduction processes to reduce NO_x emissions by the following reaction [Winter *et al.* 1999].

$$2/3NH_3 + NO \rightarrow 5/6N_2 + H_2O \quad (6.8)$$

High nitrogen containing fuels give relatively higher concentrations of HCN and NH_3 during combustion which can reduce already formed NO by reactions 6.6 to 6.8. Hydrocarbons form H-radicals which can also convert HCN to NH_3. Hydrocarbon radicals reduce NO to N_2 in the same way as during reburning, so called "intrinsic reburning effect" [Niksa and Cho, 1996]. Alzueta *et al.* (1997) however found that below 900 °C interaction of hydrocarbons with NO is very small. As the fluidised bed during the present work was operated at 800 – 900 °C, it is possible that hydrocarbon influence on the NO reduction may not be considerable.

Conversion of nitrogen to NH_3 decreases with increase in partial pressure of oxygen as NH_3 oxidizes to NO and N_2 if enough oxygen is present. With increase in oxygen partial pressure HCN increases and reaches a maximum then decreases by possible conversion of HCN to N_2O [Winter *et al* 1999] by reaction 6.7. Conversion of HCN to $NH_3$by reaction 6.6 takes place at low oxygen concentrations only [Miller and Brown, 1989]. It is well known that NH_3

and HCN can act as NO reductants or oxidants depending upon temperature "so called temperature window" and controlled by radical pools [Kristensen *et al.* 1996]. Depending upon oxygen partial pressure and concentration of radicals, temperature for maximum reduction in NO is about 900 °C [Kasuya, *et al.* 1995].

In the case of coal more HCN is produced at higher temperatures mainly by tar cracking reactions and NH_3 formation decreases [Nelson *et al*, 1992]. As NH_3 is mainly oxidized to NO, the production of more HCN than NH_3 can lead to lower NO emissions.

NO_x formation during biomass combustion at temperatures between 800 and 1100 °C is mainly due to fuel bound nitrogen [Sjaak and Jaap, 2008]. Due to the lower nitrogen content of biomass fuels, combustion of most of the biomass fuels is expected to reduce NO_x emissions. However, co-firing particularly at low co-firing ratios has resulted in, both higher and lower NO_x emissions, from biomass coal blends than those from coal alone.

Biomass fuels have a different chemical structure to coals. In biomass, nitrogen is predominantly present as aliphatic nitrogen in amino and ammonium structures. While in coal nitrogen is mostly present in aromatic structures. Moreover, biomass has higher hydrogen and lower nitrogen content than coal. That is why N_2O is hardly detected during fluidised bed combustion of biomass [Knobig *et al.* 1997] as it is converted to N_2 and OH by reacting with H by reaction 6.5.

The ratio of O to N is a describing parameter for HCN to NH_3 ratio. High O/N ratio corresponds to low HCN/NH_3 ratio [Hamalainen and Aho, 1994]. Fuels with higher O/N ratios form more OH radicals and other oxygen containing radicals who are responsible for the conversion of HCN to NH_3 [Aho *et al.* 1993]. Hydrogen is also possibly required to convert HCN to NH_3 [Winter *et al* 1999].

Ratios of H/N, O/N and O/H for all the fuels tested are given in Table 6.6. The table shows that O/N ratio for 50/50 coal-pulp blend is higher than 60/40 and 70/30 blends which can results in the formation of more NH_3 by mechanisms described above. The NH_3 can reduce NO to N_2 by reaction 6.8 thus emissions of NO for 50/50 blend should be lower as compared to the other two. However, the emissions for all the three blends are in the same range, see

Table 6.5. The table also shows that O/H ratio for the 50/50 blend is the highest than the other two. Comparatively lower amount of H in the 50/50 blend may result in lower NH_3 production by reaction 6.6 and thus reduction of NO to N_2 by reaction 6.8 is reduced. Also, higher fuel moisture content can produce more O and OH radicals which can result in lower NO emissions by reaction 6.7. As 50/50 blend has the highest moisture content, it should have the lowest NO emissions of the three blends. Moreover, nitrogen content of the 50/50 blend is lower than the other two due to lower coal proportion, thus it should give lower NO emissions. The influence of all of these parameters alongside moisture variation may have balanced and the resultant NO_x emissions don't show significant variations. Therefore, due to the influence of other parameters it is not possible to discuss the results in relation to these elemental ratios.

Table 6.6: H/N, O/N and O/H ratios of the fuels tested on DAF basis

	H/N	O/N	O/H
Thoresby Singles Coal	1.1	4.2	3.8
Wood Pellets	60.3	434.1	7.2
50/50 Coal-Pellets Blend	5.62	27.28	4.85
Wood Chips	7.9	34.2	4.4
15%M Blend	4.38	14.92	3.4
55%M Blend	3.64	10.82	2.98
Sugar Beet Pulp	12.3	74.5	6.1
50/50 Coal-Pulp Blend	3.33	10.16	3.05
60/40 Coal-Pulp Blend	3.16	8.5	2.69
70/30 Coal-Pulp Blend	2.82	6.75	2.4

Note: analysis of Thoresby coal and pressed sugar beet pulp were provided by British Sugar while those of wood chips and wood pellets are taken from literature.

Effect of fuel characteristics and operating conditions on NO_x emissions is discussed hereunder.

a) Effect of Moisture:

The effect of moisture on NO_x emissions is not found to be significant during co-firing wood chips and pressed pulp with coal. During coal-wood chips co-firing tests it is observed that during 15%M blend (10.3% moisture) combustion NO_x emissions varied from 1218 to 1436mg/Nm^3 (corrected to 6% O_2). During 55%M (moisture 30.3%) combustion the emissions varied from 1236 to 1468mg/Nm^3 (corrected to 6% O_2).Proportion of coal in 55%M blend is higher and thus higher nitrogen content than 15%M blend therefore NO_x emissions for 55%M blend should have been higher. However, the emissions for both of the blends are in the same range which may be due to higher moisture content of 55%M blend which can result in reducing NO_x emissions by reaction 6.7 and thus the effect of both of these parameters acting opposite to each other alongside other parameters is almost balanced. Increase in moisture content results in reduction in NO_x emissions due to reduced fuel nitrogen as well as lower bed temperatures. Concentration of NO_x decreases for different moisture contents and excess air values by reactions of NO with fuel carbon and CO on the surface of chars. However, in a study of NO_x emissions from co-firing saw dust (moisture content 51 – 63%) and Polish and Russian coals (moisture content 9 – 13% and 9 – 11%, respectively), Savolainen (2003) found that high moisture content in fuel tends to delay ignition and overall NO_x emissions could be higher than with pure coal. The net effect of delayed ignition to increase NO_x and lower nitrogen content, lower temperatures and reactions on the char surface to decrease NO_x is probably balanced and no considerable effect of moisture on NO_x emissions is observed during the tests.

The effect of CO on NO_x reduction is also observed by Kuprianov *et al.* (2010) and have shown by firing rice husk of different moisture contents in a swirling fluidised bed combustor that NO_x emissions can be reduced by increasing the moisture content of the fuel. At higher moisture contents NO_x emissions are lower but combustion stability is compromised. The effect of moisture on NO_x emissions was also investigated by Kouprianov and Permchart (2003) who found that NO_x emissions for 33.6% moisture saw dust were lower than 15.9% moisture saw dust under similar operating conditions. However, during the present study two fuels are blended in different proportions. Thus, not only the moisture content but other characteristics also change and thus it is not possible to distinguish the effect of moisture from other influencing parameters.

With increase in moisture content of fuel more O and OH radicals are produced. With increase in radicals more NCO is produced which converts NO to N_2O by reaction 6.7 and thus NO_x emissions are reduced.However, during present study NO_x emissions for different coal-pulp blends are found to be in the same range (1200 – 1600 mg/Nm^3) indicating that the effect of moisture on NO_x emissions is not noticeable or is balanced by the influence of other operating parameters.

b) The Effect of Bed Temperature:

The effect of temperature on NO_x emissions for different fuels is observed to be different. For coal only firing and coal-pellets co-firing the emissions found to be slightly increased with increase in bed temperature. Effect of temperature is more pronounced for the blend as compared to coal alone. Emissions of NO_x increase with increase in bed temperature for coal due to decreased influence of char at higher temperatures. At higher bed temperatures char is consumed quicker and NO_x reduction by char is lower and emissions increase. Moreover, at higher bed temperature combustion rate is higher and production rate of radicals increases [Kilpinen and Hupa, 1991] which can result in increased conversion of nitrogen to NO. Emissions of NO_x with 15%M blend are found to decrease with increase in bed temperature. The emissions decreased from 1436 to 1218 mg/Nm^3 (corrected to 6% O_2) when bed temperature is increased from at 785 to 895 °C. Similar observations were made by Amand and Leckner, (1988) and Oka and Anthony, (2003) who found that combustion temperature has the largest effect on NO_x and N_2O emissions during fluidised bed combustion. With an increase in bed temperature concentration of NO_x increases while that of N_2O decreases. Braun *et al*, (1990 and 1991) also observed effect of bed temperature on NO_x emissions and found that when bed temperature was increased concentration of NO_x increased from 0 to 150 mg/m^3 while those of N_2O decreased from 250 to 100 mg/m^3 for a low volatile coal. However, with 55%M blend the emissions are not found to be significantly changed with changes in bed temperature. Therefore, the effect of reduced char and increased conversion of NO to N_2O alongside other parameters is almost balanced.

During co-firing coal-pulp blends NO_x emissions found to be decreased with increase in bed temperature. Bed temperature increases with decrease in excess air. This reduced air flow results in lower oxygen availability to convert NH_3 to NO by reaction 6.4 and thus the

emissions are reduced. Although the data is scattered, the effect of temperature on NO_x emissions is more pronounced at higher pulp proportions in the blend possibly due to increase in moisture content of the blend with increase in pulp proportion.During 50/50 blend combustion the emissions increased from 1256 to 1488 mg/Nm^3 (corrected to 6% O_2) with decrease in bed temperature from 865 to 790 °C. Similarly, during 60/40 blend combustion the emissions increased from 1173 to 1454 mg/Nm^3 (corrected to 6% O_2) with decrease in bed temperature from 910 to 770 °C and during 70/30 blend combustion the emissions increased from 1169 to 1530 mg/Nm^3 (corrected to 6% O_2) with decrease in bed temperature from 925 to 798 °C. At lower bed temperature the emissions for all the three blends are not very much different but at higher bed temperatures the emissions show more variation with changes in bed temperature with 50/50 blend the most effected. Thus, the effect of bed temperature is more pronounced at higher bed temperatures compared to that at lower bed temperatures. This may be due to the production of more O and OH radicals, at higher temperatures and higher moisture contents, which can convert NO to N_2 by reactions 6.6 and 6.7.

c) Effect of Volatiles and Char:

Bed solids especially char play a key role in the destruction of NO_x and N_2O and formation of molecular nitrogen. With lower volatile content fuels, char concentration in the bed is increased creating favourable conditions for destruction of NO_x and formation of molecular nitrogen [Oka and Anthony, 2003]. Effect of volatiles and char content of fuel on NO_x is observed during coal-pellets co-firing. Comparison of results for pellets and coal only firing shows that NO_x emissions for 50/50 coal-pellets blend are lower than the average value obtained during single fuels firing although nitrogen content of the blend is almost half of that of the coal. This is possibly due to lower volatiles to fixed carbon ratio (1.51) of the blend than the average value (2.58) of the individual fuels, see Table 6.7. This means that amount of char input is relatively higher which can result in lower NO_x emissions. Similar results were obtained by Suksankraisorn *et al.* (2003) who found that with increase in MSW waste fraction in coal-waste blend fewer particles of char are available in the bed and thus there are less chances of NO reduction by carbon. Thus, emissions of NO increase slightly, as mass fraction of MSW in the blendis increased. Leckner and Karlsson (1993) also observed

that NO_x emissions increase with decrease in coal mass fraction during co-firing coal and wood and shownthat NO_x emissions increased to a maximum at about 20% – 30% coal by weight.

There is conflicting information in the literature on the effect of volatiles on NO_x emissions. Oka and Anthony, (2003) described that combustion of high volatile, high nitrogen content coal generally gives lower NO_x emissions. On the other hand Braun *et al*, (1990 and 1991) observed that during the combustion of high volatile coal more NO_x is formed. However, Moritomi, *et al.* (1991) found that NO_x and N_2O emissions are not affected by the volatile content of the coal in a bubbling fluidised bed.

Emissions for coal-pulp blends do not show a noticeable effect of volatiles on NO_x emissions. The emissions for all the coal-pulp blends are almost in the same range despite change in pulp proportion in the blends. However, it should be noted here that the ratio of volatiles to fixed carbon for the blends are not very much different due to very low dry mass contribution of pulp in the blends, see Table 6.7. Thus small variation of volatiles does not show significant changes in NO_x emissions. Similar observation were made by Braun, (1990) who observed constant NO_x emissions with the small rise in freeboard temperature due to combustion of volatiles in the freeboard. Similar results were obtained by Moritomi, *et al.*, (1991).

Also nitrogen in different fuels is present in different forms. The type of nitrogen compound produced during combustion depends upon nitrogen species present in the fuel and thus effects NO_x emissions. During fluidised bed combustion more of the nitrogen present in biomass fuels is released as NO_x as compared to coal [Leckner and Karlsson, 1993]. Thus NO_x emissions should behigher when co-firing biomass with coal as compared to those obtained when firing coal alone. However, due to lower nitrogen content of biomass than coal, lower loading and higher reactivity of biomass char [Tillman, 1991] opposite trend is observed.

Table 6.7: Volatiles and Fixed carbon content of Fuels and blends tested (% of combustible matter)

	Volatiles (%)	Fixed carbon (%)	V/FC	Normalised V/FC with coal
Coal	38.2	61.8	0.62	1
Pellets	81.94	18.06	4.54	7.32
PP	99.6	0.4	269	433.87
Chips	79.32	20.68	3.84	6.19
Coal-Chips blends				
15%M	57.82	42.18	1.37	2.21
55%M	51.6	48.4	1.07	1.73
Coal-Pellets blend				
50/50	60.23	39.77	1.51	2.44
Coal-PP blends				
50/50	52.5	47.5	1.1	1.77
60/40	48.5	51.5	0.94	1.52
70/30	45.3	54.7	0.83	1.34

d) Effect of Excess air:

During the tests it is observed that the emissions of NO_x increase with increase in excess air. Increase in excess air increases oxygen level which creates favourable conditions for the oxidation of volatile nitrogen compounds. At lower excess air NO is reduced due to the presence of fule rich conditions. During coal-wood chips co-firing tests it is observed that during 15%M blend combustion NO_x emissions varied from 1218 to 1436 mg/Nm^3 (corrected to 6% O_2) when excess air is varied from 10.3 to 13.6 % O_2 in the flue gas. The highest NO_x emissions are observed at the highest excess air level and vice versa. During 55%M combustion, however, the data is scattered and no clear trend is found. The emissions varied from 1236 to 1468 mg/Nm^3 (corrected to 6% O_2) when excess air is varied from 9.5 to 12.9% O_2 in the flue gas with the highest number (1468 mg/Nm^3) observed at 10.5% O_2 and the lowest number (1236 mg/Nm^3) observed at 11.9% O_2.

During 50/50 coal-pulp blend combustion the emissions increased from 1256 to 1488 mg/Nm^3 (corrected to 6% O_2) with increase in excess air from 9.3% to 11.5% O_2 in the flue gas. Similarly, during 60/40 coal-pulp blend combustion the emissions increased from 1173 to 1454 mg/Nm^3 (corrected to 6% O_2) with increase in excess air from 8.2% to 12.1% O_2 in the flue gas and during 70/30 coal-pulp blend combustion the emissions increased from 1169 to 1530 mg/Nm^3 (corrected to 6% O_2) with increase in excess air from 7.4% to 12% O_2 in the flue gas.

Effect of excess air on NO_x emissions is reproduced from Mahmoudi *et al.* (2010) in Figure 6.16. The figure shows that the emissions increase with increase in excess air. The effect of excess air is more pronounced at higher temperatures. Increase in NO emissionswith increase in excess air due to fuel NO_x formation mechanism was also observed by Permchart and Kouprianov, (2004). Similar observations weremade by Kuprianov *et al.* (2010) when rice husk of different moisture contents was fired in a swirling fluidised bed combustor. Moritomi *et al.*, (1991) observed that increase in excess air causes a significant increase in NO_x emissions. Kouprianov and Permchart (2003) also observed similar phenomenon and found by firing saw dust in conical fluidised bed that NO_x emissions varied from 180 – 200 ppm corresponding to higher values at higher excess air and temperature.

Braun (1990) measured increased NO_x emissions from a 4 MW_{th} fluidised bed combustor with increase in excess air (30 – 270%) with almost constant bed temperature (800 – 825 °C). Bramer and Valk (1990) observed by burning Columbia (volatiles 32.8%) and Australia (volatiles 15.9%) coals in a 1 MW_{th} furnace that when excess air in the bed was changed from 1.2 to 0.8, NO_x emissions reduced from 550 to 375 mg/m^3.

Oka and Anthony (2003) found that an increase in excess air simultaneously affects the formation and destruction of nitrogen oxides. During combustion typically 20 – 40% of fuel bound nitrogen is converted to NO_x [Hoy and Gill, 1987]. Conversion of fuel nitrogen increases with increase in equivalence ratio and mixing [Pohl and Sarofim, 1976]. Fuel NO_x are not very much sensitive to temperature but are sensitive to mixing. During pulverized coal combustion at 2480K, Pershing and Wendt (1977) however, found that 75% of the total NO_x produced came from fuel NO_x mechanism. As fluidised bed provides excellent mixing

of fuel and air, it can be assumed that all the NO_x formed are from fuel nitrogen [Mahmoudi *et al.* 2010].

Effect of excess air on NO_x emissions is also influenced by the presence of Ca in the fuel. Catalytic effect of CaO leads to significant NO_x emission differences from combustion in fluidised beds using silica bed [Amand and Leckner, 1988]. Presence of CaO may result in increased NO_x formation if excess oxygen is present [Leckner and Amand, 1987]. During present study with coal-pulp blends it is found that NO_x emissions tend to increase with increase in excess air which may be due to combined effect of presence of Ca contributed by pulp as well as presence of oxygen.

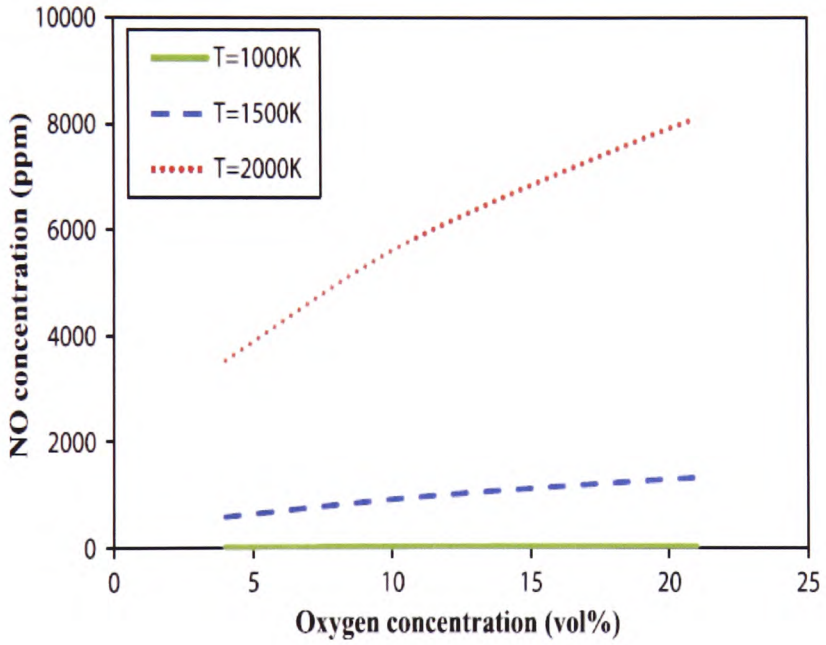


Figure 6.16: NO formation as a function of O_2 concentration at various temperatures and at a fixed reaction time of 4s, typical of CFBC [Mahmoudi, *et al.* 2010]

However, Duan *et al.* (2012) observed decrease in NO_x emissions with increase in excess air. According to them it may be due to lower availability of CO at higher excess air and thus NO_x reduction by CO by reaction 6.9 is comparatively lower.

$$2NO + 2CO \rightarrow 2CO_2 + N_2 \quad (6.9)$$

e) Effect of measurement point:

The measured emissions of NO_x may also be influenced by the height at which measurement is taken. Kuprianov *et al.* (2006) found that NO_x concentration was maximum at a certain height in the combustor and decreased after that. They found that in the freeboard region NO_x concentration decreased due to reduction of NO_x by different reactions. Kouprianov and Permchart (2003) also observed that NO_x concentration vary along the freeboard height due to reduction process.

Fuel NO_x formation reactions are most likely to occur in the bottom part of the fluidised bed combustor [Kouprianov and Permchart, 2003]. Ammonia (NH_3) released in volatiles and formed from HCN reduces NO_x into nitrogen and water in the upper part of the combustor [Winter *et al.* 1999]. Highest decomposition rate of CO and NO is found to occur in the splash zone of the combustor [Kuprianov *et al.* 2010].

Thus it is possible that NO_x emission readings could have been off the optimum values which could have been achieved as the measurements were taken at 0.73m above the bed. Also, NO_x formation and destruction reactions are different for different fuels and at a particular point in the combustor emissions could have been different from optimum.

f) Effect of Co-Firing:

The emissions of NO_x depend upon nitrogen content of the fuel. As biomass fuels have lower nitrogen content than coal, NO_x emissions during co-firing are found to be lower for all the pellets, chips and pulp blends with coal as compared to coal alone. The emissions from wood pellets firing (200 – 400 mg/Nm^3, corrected to 6% O_2) are the lowest and are 4 – 6 times lower than those from coal (1600 – 1800 mg/Nm^3, corrected to 6% O_2). During coal-wood

chips (as received as well as with high moisture) co-firing NO_x emissions (1200 – 1500 mg/Nm^3, corrected to 6% O_2) are found to be lower than coal but very much higher than wood pellets. This may be due to higher nitrogen content of wood chips (0.95% with 15% moisture and 0.51% with 55% moisture) than wood pellets (0.08%).The rate of formation of NO_x, HCN and NH_3 oxidation was higher in the bed resulting in higher NO_x levels. The emissions from the combustion of coal-pulp blends are also lower (1200 – 1600 mg/Nm^3, corrected to 6% O_2) than coal due to lower nitrogen content of pulp (0.14%) but the difference is small due to very low dry mass contribution of pulp (11.6% in 70/30 blend and 23.5% in 50/50 blend).

Similar observations were made by Kuprianov *et al.* (2006) who found that higher nitrogen content of rice husk in its blend with bagasse increases the overall nitrogen content of the blend when its proportion is increased. They found that emissions of NO_x from conventional fluidised beds burning rice husk are high (100 – 180 ppm at 20 – 100% excess air) due to higher nitrogen content in the fuel. Chakritthakul and Kuprianov (2011) observed optimum performance of swirling fluidised bed combustor firing eucalyptus bark and rubberwood sawdust in a ratio of 3:1 (sawdust:bark) at an excess air level of 50 – 55%.

6.8.2 SO_2 Emissions:

Emissions of SO_2 normalised to 6% O_2 for different fuels tested are summarised in Table 6.8. The emissions for all the solid fuels and combinations of fuels, except wood pellets, are considerably higher than limits set out by EU Directive [EU Directive, 2010/75/EU], see Table 6.1. However, because of the research nature of the project, no control measures have been adapted as are used in the industry on full scale plants.

The data shows that the emissions are the highest for coal and the lowest for pellets. The emissions for coal-pellets and coal-chips blends are higher than for pellets alone due to higher sulphur content of coal. However the results of emissions for different coal-pulp blends are interesting and vary considerably with change in blending ratio. The emissions decrease with increase in pulp proportion in the blend despite very little contribution of dry matter from pulp. This may be due to increase in the moisture content of the blend with increase in pulp ratio. The effect of different parameters on SO_2 emissions is described hereunder.

a) Effect of Moisture and Ca/S ratio:

During coal-pulp blends combustion the emissions of $SO_2$are decreased with increase in pulp proportion in the blend. The emissions varied between 500 – 1000, 1000 – 1500 and 1600 – 2400 mg/Nm^3 (corrected to 6% O_2) for 50/50, 60/40 and 70/30 coal-pulp blends, respectively. The efficiency of sulphur fixation in the ash depends upon the concentration of alkaline earth metals, especially calcium, in the ash. Calcium contained in the coal ash can capture a considerable amount of SO_2 [Raymant, 1989]. Ash from certain coal types can capture above 90% of sulphur [Zhang, *et al.* 1991]. Generally, de-sulphurisation efficiency increases with increases in the Ca/S ratio [Oka and Anthony, 2003]. Analysis shows that Ca/S ratio of pulp is 143 times and of 50/50 coal-pulp blend is 10 times that of coal. Ca/S ratio increases with increase in pulp proportion in the blends due to its higher Ca and lower S content. This could be one of the possible reasons for lower SO_2 emissions with increase in pulp proportion in the blends. De-sulphurisation efficiency increases with increase in contact time between SO_2 and CaO. Thus higher bed height may result in decreased SO_2 emissions [Oka and Anthony, 2003]. Static bed height in the present study was only 200 mm and thus it is anticipated that maximum sulphur capture efficiency might have not been achieved. The decrease in SO_2 emissions with increase in pulp proportion in coal-pulp blends may also be due to increase in moisture content. Presence of moisture can convert SO_2 to H_2SO_4 by mechanisms explained previously in this chapter.

The Ca/S ratio for 15%M (0.28) is higher than 55%M (0.23), see Table 6.8, but SO_2 emissions for 15%M (1000 – 1500 mg/Nm^3) are higher than 55%M (750 – 1050 mg/Nm^3) possibly due to higher moisture content of the latter (30.3%) than the former (10.3%) which can convert SO_2 to H_2SO_4. The emissions of SO_2 for the 70/30 coal-pulp blend (1800 – 2400 mg/Nm^3) are considerably higher than 15%M blend (1000 – 1500 mg/Nm^3) possibly due to higher Ca/S ratio for 15%M blend (0.28) than 70/30 coal-pulp blend (0.25). Also for 55%M blend SO_2 emissions are lower than 70/30 coal-pulp blend although Ca/S ratio and moisture content are similar. This is possibly due to higher biomass contribution in the case of coal-wood chips blends (15%M and 55%M blends) as compared to coal-pulp blends which tends to retain S in ash. This is also evidenced by lower SO_2 emissions in the case of coal-pellets

blend than coal although Ca/S ratios are almost equal. Thus higher proportion of biomass in coal-biomass blend tends to lower SO_2 emissions.

However, higher amount of CaO does not necessarily mean a higher sulphur capture efficiency as Fe_2O_3 can have a catalytic effect on the reaction of CaO and SO_2 [Yeh at al. 1987]. Zhang *et al.* (1991) concluded by a comparative study on six different facilities and nine different coals that it is not possible to determine a general relationship between de-sulphurisation efficiency and Ca/S ratio. Moreover, microstructure of calcium also affects its sulphur capture efficiency. Larger specific surface area CaO has more capability to capture SO_2 as compared to that having smaller specific surface area [Duan *et al.* 2010]. It is possible that CaO present in different fuels may have different pore structures and thus different sulphur capture efficiency and may be a possible reason for variations and data scatter in sulphur emissions during tests with different fuels.

Table 6.8: Comparison of SO_2 emissions for Fuels and blends tested

Fuel	SO_2 (mg/Nm^3 at 6% O_2)	Ca/S	
		Mass	Molar
Coal	2500 – 2750	0.06	0.05
Pellets	150 – 250	0.13	0.10
Coal-Pellets blend (50/50)	600 – 1100	0.08	0.06
Coal-15% moisture Chips blend (50/50)	1000 – 1500	0.35	0.28
Coal-55% moisture Chips blend (50/50)	750 – 1050	0.29	0.23
Coal-Pressed Pulp blend (50/50)	600 – 1200	0.61	0.49
Coal-Pressed Pulp blend (60/40)	1000 – 1500	0.44	0.35
Coal-Pressed pulp blend (70/30)	1800 – 2400	0.31	0.25

b) Effect of Excess air:

Effect of excess air on SO_2 emissions is plotted in Figures 6.17 and 6.18 for 50/50 coal-pulp and 15%M blends, respectively. The figures show that the emissions decrease with increase in excess air. This shows that sulphur retention is increased at higher excess air levels. During 50/50 coal-pulp blend combustion SO_2 emissions decreased from around 900 to 600 mg/Nm^3, a reduction of around 33%, when excess air is increased from 8.5% to 10.8% O_2 in the flue gas. During 15%M blend combustion SO_2 emissions decreased from 1500 to 1200 mg/Nm^3, a reduction of 25%, when excess air is increased from 10.3% to 13.7% O_2. The higher reduction in the case of 50/50 coal-pulp blend as compared to 15%M blend, although the excess air level and its variation range for the former is lower, may be due to higher moisture content of the former (38.3%) than the latter (10.3%). Similar results were obtained by Khan and Gibbs (1991) who observed 5% – 10% reduction in SO_2 emissions when excess air was increased from 1.3 to 1.4. Oka and Anthony, (2003) also observed that increase in the amount of excess air results in the increased de-sulphurisation efficiency.

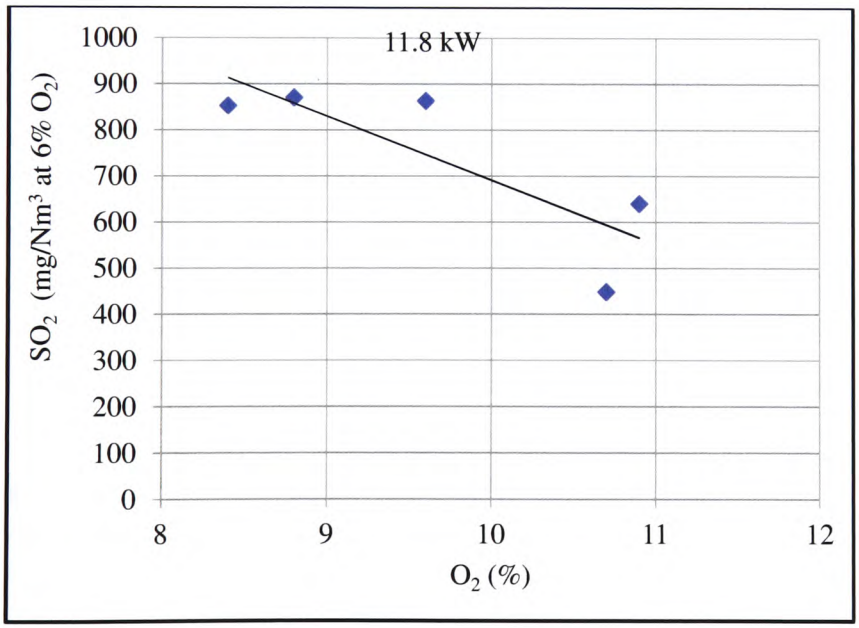


Figure 6.17: SO_2 vs. O_2 for 50/50 coal-pulp blend

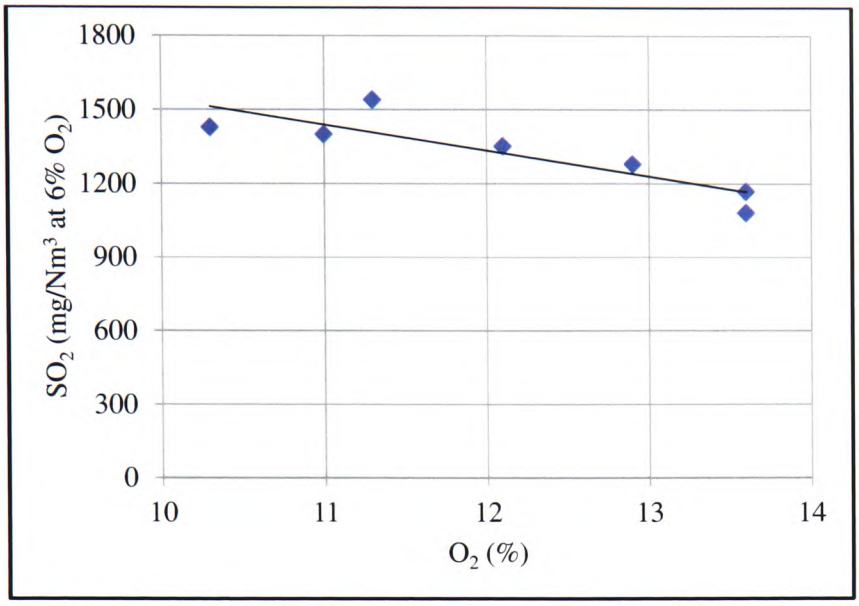


Figure 6.18: SO_2 vs. O_2 for 15%M blend

Split between primary and secondary air also effects de-sulphurisation efficiency. Wormgoor *et al.* (1991) observed that SO_2 retention decreased from 90% to 80% when primary air share was decreased from 1.2 to 0.87. However, during present study no secondary air was used therefore it is not possible to comment on the effect of air split on SO_2 emissions.

Increase in excess air levels increases fluidising velocity. So an intuitive conclusion is that sulphur emissions decrease with increase in fluidising velocity. However, not only that fluidising velocity is influenced by operating temperature, it also influences other variables such as residence time and mixing. Higher fluidisation velocity reduces residence time of gas in the bed and freeboard but increases intensity of mixing and attrition. Therefore, it is difficult to determine the effect of fluidisation velocity on sulphur capture. However, Oka and Anthony, (2003) stated that normally, higher SO_2 emissions should be expected at increased fluidisation velocity. Similar results were witnessed by Valk *et al.* (1989) who obtained lower de-sulphurisation efficiency with higher fluidisation velocity. However, Zhang *et al.* (1989) observed that fluidisation velocity does not significantly affect sulphur retention in fluidised beds. As explained earlier, during present study SO_2 emissions observed to be decreased with increase in fluidising velocity.

c) Effect of Bed Temperature:

Emissions of SO_2 are also affected by changes in bed temperature. During present study it is found that SO_2 emissions increased slightly with increase in bed temperature for low moisture fuels e.g. coal, pellets and their blend. The emissions with coal, pellets and their 50/50 blend increased from 2500 to 2750 mg/Nm^3, 170 to 266 mg/Nm^3 and from 990 to 1100 mg/Nm^3 when bed temperature increased from 760 to 910 °C, 773 to 899 °C and 748 to 883 °C, respectively.

With higher moisture fuels e.g. coal-pulp blends effect of bed temperature on SO_2 emissions is more pronounced and the emissions found to be higher at higher bed temperatures. The emissions increased from around 600 to 1200 mg/Nm^3, 1000 to 1500 mg/Nm^3 and 1800 to 2400 mg/Nm^3 with increase in bed temperature from 780 to 885 °C, 810 to 860 °C and 825 to 925 °C during firing of 50/50, 60/40 and 70/30 coal-pulp blends, respectively. Increased emissions of SO_2 with temperature may be due to decomposition of calcium sulphate ($CaSO_4$), present in the fuel or formed by forward reaction (6.10) in the early stages at lower temperatures, into CaO and SO_2 by the following reverse reaction [Duan *et al.* 2010].

$$2CaO + 2SO_2 + O_2 \leftarrow 2CaSO_4 \qquad (6.10)$$

The temperature at which maximum sulphur capture efficiency occurs is 800 °C – 900 °C [Oka and Anthony, 2003] which is within fluidised bed operating temperature range. Change in sulphation efficiency with variation in temperature in the vicinity of the optimum temperature is not much. The optimum temperature for maximum SO_2 capture varies from coal to coal [Fernandez *et al.* 1989] and from unit to unit. Leckner and Amand, (1987) have shown that sulphation efficiency reduces significantly when temperature is below 780 °C or above 960 °C. As most of the experiments performed during this study were in this temperature range, it is expected that sulphation efficiency is not very much affected.

d) Effect of Co-Firing:

Emissions of SO_2 reduce as biomass mass fraction is increased due to fuel sulphur dilution. Because of low sulphur content of the biomass fuels SO_x emissions decrease depending upon the co-firing ratio and the sulphur content of the biomass. The emissions are found to be lower when co-firing as compared to coal alone firing. An additional incremental reduction beyond the amount anticipated on the basis of fuel sulphur content is possibly due to the sulphur retention by alkali compounds in biomass ashes. During co-firing coal and pulp blends SO_2 emissions were found to be decreased with increase in biomass fraction. With wood pellets the emissions were found to be considerably lower than coal but a 50/50 blend of coal and pellets shown intermediate behaviour possibly due to lower sulphur content of pellets.

During present study effect of biomass volatiles on SO_2 emissions was not found to be in line with the findings of Suksankraisorn *et al.* (2003). They observed that fuel sulphur conversion increases with MSW mass fraction due to high volatile content creating reducing conditions around the dense bed. This inhibits the sulphur capture in the bed and H_2S and CO_s species are converted to SO_2 in the freeboard area.

The phenomenon of increased SO_2 emissions with increase in volatiles content was also observed by Oka and Anthony, (2003) who stated that increase in the amount of volatiles may increase SO_2 emissions as SO_2 and H_2S are released and formed during de-volatilisation process. However during present study opposite effect was observed when pellets and low moisture chips were co-fired with coal. The SO_2 emissions during co-firing were lower than expected, showing that effect of volatiles from pellets was not prominent. However, it is possible that sulphur was retained in the pellets ash resulting in lower SO_2 emissions.

It is not possible to comment on the effect of volatiles on SO_2 emissions for high moisture chips and pulp blends with coal due to influence of moisture on the emissions. Moreover, energy contribution of pressed pulp in the blends is very low 4.4 – 9.6%. Thus volatiles contribution of pulp in the blends is not significant and may have little effect, if any, on the emissions.

Above discussion shows that different biomass fuels behave differently when co-fired. Emissions of SO_2 as a function of biomass proportion in coal-biomass blend as reported by Leckner and Karlsson, (1992) are reproduced in Figure 6.19. The figure shows that SO_2 emissions decrease with increase in biomass proportion except sewage sludge where trend is reverse. Thus the influence of volatiles on SO_2 emissions depends upon type of biomass fuel as nature of volatiles varies from fuel to fuel.

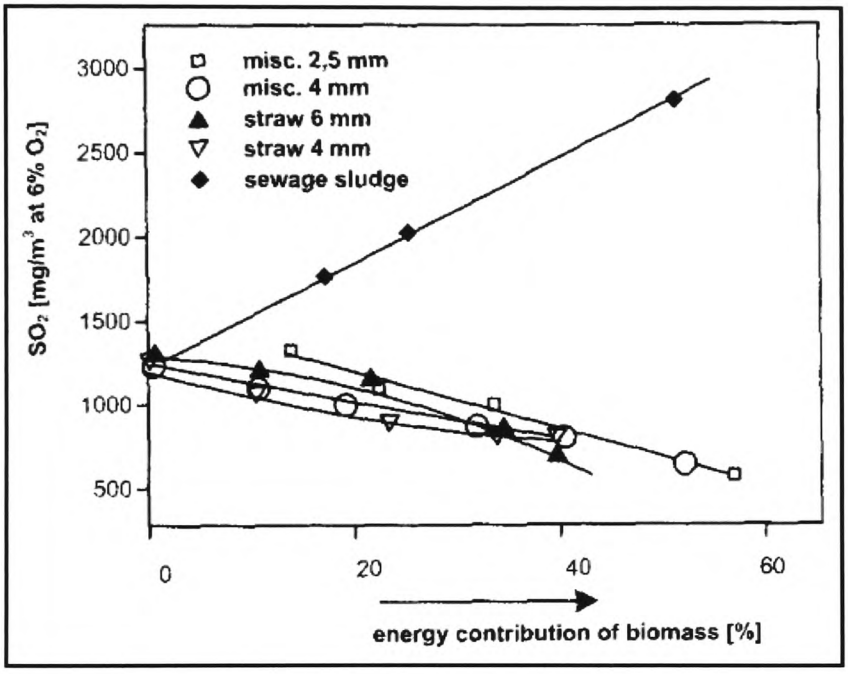


Figure 6.19: Influence of co-firing various biomass fuels on SO_2 emissions [Leckner and Karlsson, 1992]

6.8.3 CO Emissions:

Measurement of CO emissions is a good indicator of the quality of combustion and provides reasonably good surrogate for the organic species. Measurement of CO emissions is cheaper and simpler than measurement of the more complex organic species. Emission levels of these pollutants can be controlled by making sure that co-firing does not have a significant impact on emissions i.e. the particle size and moisture content of the biomass are acceptable, the

method of introduction of biomass is appropriate and system is designed and operated properly.

Emissions of CO can be controlled by adjusting the air to fuel ratio and by proper mixing of air and fuel. During de-volatilisation of biomass, CO, CO_2 and CH_4 are released and contribute to the formation of CO [Werther *et al.* 2000]. Heterogeneous reactions of CO_2 and H_2O with carbon most likely result in the formation of CO as temperature in the FBC is lower than 1000 °C [Tillman *et al.* 1981]. In the bottom part of fluidised bed combustor de-volatilisation and primary reactions are dominant while in the upper part post combustion CO is consumed by its oxidisation by O_2 as well as OH radicals [Kouprianov and Permchart, 2003].

Emissions caused by incomplete combustion are mainly a result of inadequate mixing of air and fuel, lack of available oxygen, too short residence time, too low combustion temperature and too low radical concentration specially OH. These variables need to be optimized to reduce emissions caused by incomplete combustion [Sjaak and Jaap, 2008]. The emissions of CO, converted to 6% O_2, from the combustion of different fuels and their blends are given in Table 6.9. The effect of fuel characteristics and operating conditions on CO emissions is discussed in the following paragraphs.

a) Effect of Moisture

Moisture content influences the combustion behaviour, adiabatic flame temperature and volume of the flue gas produced per unit energy. Wet fuels need longer residence time for drying stage thus higher bed volume is required in order to adjust the temperature control system of the bed properly and to design the volume of the furnace in a way that ensures a sufficient residence time of the flue gas in the hot bed for complete combustion. Increase in moisture content of the fuel reduces maximum possible achieveable temperature and therefore opportunity for preventing emissions as a result of incomplete combustion is reduced [Sjaak and Jaap, 2008]. Therefore, combustors designed for low moisture fuels, e.g. coal used in the present study, can not be used for high moisture fuels without significantly compromising their performance.

Table 6.9: Comparison of CO emissions for Fuels and blends tested

Fuel	CO (ppm), corrected to 6% O_2
Coal	500 – 1800
Pellets	800 – 1800
Coal-Pellets blend (50/50)	800 – 1400
Coal-15% moisture Chips blend (50/50)	1000 – 2800
Coal-55% moisture Chips blend (50/50)	1200 – 2200
Coal-Pressed Pulp blend (50/50)	600 – 1400
Coal-Pressed Pulp blend (60/40)	1200 – 2900
Coal-Pressed pulp blend (70/30)	1000 – 2500

During coal-pulp blends CO emissions (normalised to 6% O_2) were found to be above 500 ppm for all the conditions tested. The emission ranges observed for the coal-pulp blends are 600 – 1400 for ppm for 50/50 blend, 1200 – 2900 for 60/40 blend and 1000 – 2500 for 70/30 blend. However, for a fixed excess air level, CO emissions found to be decreased with increase in pulp proportion in the blend despite increase in moisture. For example, at 10% O_2 in the flue gas, CO emissions for 50/50 blend (moisture content 38.3%) are 750 ppm, for 60/40 blend (moisture content 31.8%) are 1300 ppm and for 70/70 blend (moisture content 25.2%) are 1600 ppm. This is possibly due to delayed evolution of volatiles with increase in moisture. Increase in moisture results in increase in residence time and thus more time for the fuel to burn resulting in lower CO emissions. It could also be due to higher CO reduction by increased OH radical produced at higher fuel moisture content. Similar observations were made by Kuprianov *et al.* (2010) who found that when moisture content was increased from 8.4 to 25%, CO emissions reduced from 4000 to 3000 ppm.

Emissions of CO are found to be dependent on biomass fraction in coal-biomass blends. Moreover the emissions were found to be lower with coal as compared to coal-pellets blend. When high moisture biomass is co-fired with coal CO emissions are found to be increasing with increase in coal proportion in the blend. For example, CO emissions for 50/50 coal-pellets blend combustion are higher than those for coal only combustion. The emissions varied from 800 to 1400 ppm for coal-pellets blend andfrom 500 – 1800 for coal over the

range of operating conditions tested with most of the data for coal is between 500 and 1400 ppm. Similar observations were made by Cliffe and Patumsawad (2001) who found that CO emissions at 10% olive oil waste in coal were higher and bed temperature was lower than 100% coal at the same excess air level as biomass has higher reactivity than coal. At 20% olive oil waste content in coal CO emissions were higher than 10% olive oil waste in coal or coal alone. This was due to heat being used to evaporate increased moisture content resulting in lower reaction rate and lower temperatures in the freeboard. However, Suksankraisorn *et al.* (2003) found lower CO emissions for coal-MSW blend as compared to coal. They observed that emissions of CO were below 100 ppm when simulated MSW with 60% moisture was co-fired with coal in comparison to coal firing which gave 300 ppm CO and were found to be insensitive to waste fraction in the waste coal blend.

Kuprianov *et al.* (2010) have shown by firing rice husk of different moisture contents (8.4% – 35%) in a swirling fluidised bed combustor that CO emissions can be controlled at below 350 ppm if excess air is above 40% (around 6% O_2). However, during present study CO emissions for all the tests were higher than 500 ppm when normalised to 6% O_2 which is equivalent to around 800 mg/Nm^3. The lower emissions achieved by Kuprianov *et al.* (2010) were possibly due to swirling nature of the combustor which gives better mixing thus oxygen access to unburned carbon and due to air staging as they also used secondary air.

It is observed that influence of moisture on CO emissions is more pronounced at lower excess air levels. With increase in excess air, difference in CO emissions is found to be lower at different moisture contents. At lower excess air levels CO emissions are higher due to higher wet oxidation of char at elevated moisture. For example, when O_2 level increased from 9% to 11%, CO emissions are found to be decreased from 1200 to 750 ppm, from 1800 to 1000 ppm and from 2500 to 1500 ppm for 50/50, 60/40 and 70/30 coal-pulp blends, respectively. This represents CO reductions of 450, 800 and 1000 ppm, respectively.

Similar observation was found by Kuprianov *et al.* (2010) that at moisture content below 40%, CO emissions are strongly influenced by excess air and fuel moisture content. When moisture content increased from 25% to 35%, CO emissions increased from 3000 to 7000 ppm at 20% excess air. When excess air was increased from 40% to 60% CO emissions were reduced for the range of moisture contents tested. This was thought to be caused by sub-

stoichiometric primary air. However, CO emissions were always found to be below 3000 ppm possibly due to higher excess air used during the tests. During present work these conditions of very low excess air were not tested due to safety reasons as the fluidised bed combustor was situated indoors and leakage of CO into the laboratory could have serious implications. Even then, as can be observed from Table 6.8, emissions of CO for all the fuels and blends over the range of experimental conditions tested are lower than 3000 ppm.

Dependence of CO emissions on moisture content and excess air was also investigated by Kaewklum *et al.* (2007). When firing rice husk of different moisture contents in a conical fluidised bed at different excess air levels they found that there was a maximum value for CO emissions which was different for different moisture contents and the highest value of CO maximum was found at highest moisture content. Similarly, Kuprianov *et al.* (2006) and Kouprianov and Permchart, (2003) observed that CO emissions increase with increase in moisture content of the fuel in contrast to the observation made during present study which shows that CO emissions decrease with increase in moisture. They found by co-firing rice husk and sugar cane bagasse that highest CO emissions were at highest mass fraction of bagasse in the fuel blend which corresponds to highest moisture content of the fuel blends tested. This could be due to lower temperatures resulting in higher CO/CO_2 ratio in carbon oxidation or due to enhanced char oxidation to CO due to higher concentration of water vapour. During present study CO emissions were found to be lower for 50/50 coal-pulp blend (representing the highest moisture content of the three blends) as compared to 60/40 and 70/30 blends, possibly due to delayed and slow evolution of volatiles. Also during coal-pulp blends firing major proportion of the blends was constituted of coal. The coal has low volatiles and more char which stays in the bed until combusted. But during bagasse and rice husk co-firing study conducted by Kuprianov *et al.* (2006) both fuels were biomass therefore it is possible that the higher CO emissions may be due to the amount of volatiles present which may have evolved suddenly and left the bed without burning.

Fluctuations in CO emissions are due to possible feed flow variations by screw feeder. For example, the emissions varied from 600 to 1400 ppm, from 1200 to 2900 ppm and from 1000 to 2500 ppm for 50/50, 60/40 and 70/30 coal-pulp blends, respectively. The variations may be as a result of poor mixing of the blends or possible bridging in the hopper which could have influenced feed flow rates. The fluctuations were also observed by Sami *et al.* (2001),

Abelha *et al.* (2003) and Ghani *et al.* (2009). The fluctuations are higher in the present case possibly due to higher moisture content of fuels. When a batch of high moisture fuel enters the bed the particles of the fuel need to be heated and dried first. While this occurs oxygen is not consumed and result is higher CO emissions [Ghani *et al.*, 2009].

b) Effect of Excess air:

During most of the tests with different fuels in this study CO emissions are found to be affected by excess air. The emissions first decrease and then increase with minimum values observed at O_2 levels between 12 and 13.5%. At low excess air levels, CO emissions are higher as a result of incomplete combustion due to lack of oxygen availability. As the air flow is increased CO emissions decrease due to better mixing and oxygen availability. At even higher excess air levels CO emissions again increase possibly due to decrease in temperature which results in incomplete combustion.For example, for pellets combustion CO emissions decreased from 1700 ppm to 1150 ppm when excess air is increased from 9.9% to 12.5% O_2 in the flue gas and again increased to 1300 ppm as excess air is further increased to 13.7% O_2. Similarly, for coal-pellets blend combustion CO emissions decreased from 1300 ppm to 950 ppm when excess air is increased from 10.7% to 12.5% O_2 in the flue gas and again increased to 1100 ppm as excess air is further increased to 14% O_2.

According to Sjaak and Jaap, (2008), for each fuel moisture content there is a specific excess air ratio (λ) where CO emissions are at a minimum. Emissions of CO increase, if excess air ratio is above or below this optimum value. CO/λ characteristic depends upon moisture content. Higher fuel moisture content usually increases the optimum excess air ratio and vice versa. At fixed excess air ratio, CO emissions can increase dramatically if moisture content of the fuel varies. However, during coal-wood chips tests it is observed that with 15%M blend (moisture content 10.3%) O_2 in the flue gas for minimum CO emissions is 13.5% but for 55%M blend (moisture content 30.3%) it is 12.5% which is contradicting the observations of Sjaak and Jaap. At a fixed excess air level, the emissions are higher at lower fuel moisture content and therefore become minimum at increased excess air levels. Neverthless, by carefully controlling the combustion process, furnace can be adjusted to any fuel moisture content which ensures optimized burnout and CO emissions and optimized efficiency of the system.

The effect of excess air on CO emissions was also observed by Kouprianov and Permchart, (2003) and made similar observations when saw dust with a moisture content of 33.6% was fired. They found that the effect of excess air on CO emissions was very strong when excess air was 65% – 70%. When excess air was above 70% CO was independent of excess air but was slightly dependent on fuel feed rate. They found that moisture content of fuel affects CO emissions strongly. Rao and Reddy (2011), by firing rich husk, sawdust, wood waste and groundnut shells in a bubbling fluidised bed, observed that CO emissions reduced considerably with increase in excess air.

Similar observations were made by Kuprianov *et al.* (2006) by firing rice husk in a fluidised bed and found that at excess air below 40%, CO emissions were higher than 5000 ppm and strongly dependent upon excess air. At excess air above 60% CO emissions were between 600 – 1100 ppm and were independent of excess air. Preto *et al* (1987) measured CO emissions of 250 – 6250 mg/Nm^3 while Armesto *et al.* (2002) measured 200 – 2000 mg/Nm^3 by combusting rise husk in fluidised bed and attributed these differences to different operating conditions. Bed temperature, excess oxygen, residence time and flue gas mixing all effect CO emissions.

Effect of excess air on CO emissions described above was not observed by Cliffe and Patumsawad (2001) who found, by co-firing olive oil waste with coal in a fluidised bed at 10 kW, that CO emissions were between 100 and 350 ppm at 6% O_2 and that emissions of CO increased with increase in excess air due to lower bed temperature caused by higher fluidising velocities at higher excess air levels. At higher fluidising velocities CO does not have sufficient time to convert to CO_2 and thus CO emissions increase. Thus increase in excess air can work both ways. On one hand excess air can reduce CO emissions by providing more oxygen to convert CO to CO_2 and on the other hand it can increase CO emissions by increasing fluidising velocity which can force the produced CO to leave the combustor unburned. Thus, the results of the present study can be explained on the basis that at lower excess air levels CO emissions are higher due to lack of oxygen availability. When excess air is increased, CO emissions decrease because of oxygen availability which converts CO to CO_2. At even higher excess air levels, CO emissions increase due to higher fluidising velocity and lower bed temperature.

c) Effect of blending ratio:

During co-firing, CO emissions from coal-pellets blend are found to be higher than those from coal. This is possibly due to higher volatiles content of pellets. The volatiles evolve and leave the bed unburned possibly due to lower residence time. This is also observed by Leckner (2011) who stated that more oxygen is consumed, in the bottom part of the combustor, in coal combustion than for biomass. Emissions of CO from 15%M blend are found to be considerably higher than 50/50 coal-pellets blend possibly due to difficult burning of chips as compared to pellets. However, the emissions for 55%M are lower than 15%M blend possibly due to delayed ignition as a result of higher moisture content of the former. During coal-pulp blends combustion CO emissions are found to be first increasing with increase in blneding ratio (increase in the pulp proportion in the blend) and then decreasing. The emissions increase from 1000 – 2500 ppm for 70/30 blend to 1200 – 2900 for 60/40 blend possibly due to increased moisture which hinders access of oxygen to coal particles. With further increase in pulp protion the emissions decrease to 600 – 1400 ppm which may be due to delayed ignition at higher moisture content.

d) Effect of measurement point:

Emissions of CO are also affected by point of measurement as they continue to convert to CO_2 as they pass through the combustor. According to Leckner, (2011) CO emissions decrease along the flow path and become negligible at around 9m length for coal and around 14m for wood. The effect of combustor height on CO emissions was observed by Kaewklum *et al.* (2007) who found that CO concentration was found to be reduced along the combustor height due to oxidation with OH radicals and O_2. With higher value of excess air CO concentration was found to be reduced all along the combustor due to homogeneous oxidation reaction with oxygen. Similar observations were made by Kuprianov *et al.* (2010) who found significantly reduced CO concentration along the tube from 0.8 to 1 m above the distribution plate. It is also observed that higher the moisture content, higher the reduction in CO. However, from 1m to 1.5m, CO concentration increased possibly due to fuel carbon from the bottom region is transported with chars to the top region. Above 1.5m, CO concentration decreased due to reactions with oxygen and OH radicals. Kuprianov *et al.* (2006) also observed by co-firing rice husk and sugar cane bagasse that CO emissions were

maximum at a certain height in the freeboard and then decrease. As it is mentioned earlier that height of the fluidised bed at Glamorgan was limited by the height of the ceiling and the emissions were measured at only one point, at a height of 0.73m above the distributor plate. As CO is first formed and then consumed by different reactions, the values measured during these tests might not correspond to ultimate emission values. The emissions data could have been different if measurements have been taken at a higher point in the containment tube. However, they are a good indication of trends and are useful when comparing results of combustion of different fuels and fuel blends.

6.9 Uncertainties in Emissions data:

Gas phase reactions continue to occur until temperature of flue gas is dropped to 200 – 400 °C [Winter *et al.* 1999]. As mentioned earlier the emissions measurements during the tests were taken at a height of 0.73 m above the distributor plate. At this point, the flue gas temperature was relatively high and most of the time was above 700 °C. Thus, it is possible that gas phase reactions were still occurring beyond the measurement point and ultimate emissions might be somewhat different from the measured data.

6.10 Conclusions:

The results show that blending biomass with coal considerably reduces emissions of NO_x and SO_x due to lower sulphur and nitrogen content of biomass. The reduction in emissions is observed to be higher with increased biomass content in the blends. It is observed that ratio of volatiles to fixed carbon plays a key role in reducing NO_x emissions. There was no considerable effect of moisture content on NO_x emissions. However, NO_x emissions found to be increased with increase in excess air and decreased with increase in bed temperature.

Emissions of SO_2 found to be decreased with increase in biomass proportion due to increase in Ca/S ratio. Higher moisture content of fuel reduces SO_2 emissions by possibly converting them to H_2SO_4. Emissions of SO_2 found to be decreased with increase in excess air and decrease in bed temperature with more pronounced effects with higher moisture content fuels. The emissions of CO are found to be decresed first and then increased with increase in excess air. Emissions of CO are found to be increasing with increase in coal proportion in the

blend when high moisture biomass was co-fired with coal. Emissions of CO found to be decreased with increase in pulp proportion in the blend despite increase in moisture content, possibly due to delayed ignition and longer residence time in the bed.

Chapter 7
Bed Agglomeration Tests

7.1 Introduction:

One of the operational problems of the fluidised bed combustion is agglomeration leading to less fluidisation and in worst cases loss of fluidisation. In biomass combustion agglomeration and subsequent de-fluidisation is a major problem to be solved. Due to the problems occurring during the combustion of biomass, operational and maintenance costs are high. Sustainable solution to these problems is necessary to reduce these excessive costs and increase the reliability of the biomass fired combustors.

In order to understand the behaviour of sugar making process by-products during combustion in fluidised beds and their potential to cause agglomeration due to their relatively higher alkali content, especially potassium, agglomeration tests have been performed with vinasse, raffinate and pressed sugar beet pulp during co-firing with coal and/or natural gas.
First part of this chapter presents causes of agglomeration, different agglomeration mechanisms, elements which can contribute to agglomeration, agglomeration indices and potential remedies to reduce agglomeration. Second part discusses agglomeration potential and the results of muffle furnace tests of different fuels as well as the agglomeration tests in fluidised bed test rig and SEM resultsof the bed samples obtained during the tests carried out with co-firing vinasse, raffinate and sugar beet pulp. Wherever appropriate, results are also discussed in relation to information available in literature.

7.2 Agglomeration:

Agglomeration is a major operational problem in fluidised bed combustors particularly when silica sand is used as bed materials. Inorganic alkali compound especially potassium and sodium in the fuel can form low melting silicate with the bed material and can be a source of agglomeration. The K and Na content varies from fuel to fuel and is generally high in some

biomass fuels as compared to coals. However, some low rank coals may also have higher content of these troublesome substances. The alkali silicates may have melting points even lower than individual substances. Aluminosilicate materials act as glue to form agglomerates when burning high S (low rank) coal, under fluidised bed conditions [Dawson and Brown, 12992]. As a result sand particles become coated with a sticky layer of molten mass which grows bigger with time due to collisions and bigger agglomerates are formed eventually. If not recognised, the process can lead to excessive agglomeration of the bed material. Under favourable conditions fairly extensive three dimensional agglomerates can form which can lead to poor air distribution and de-fluidisation. The result could be unscheduled shutdown of the plant which can cost in terms of time and money [Bartels, *et al.* 2008].

As mentioned earlier, an important parameter for agglomeration tendency is alkali content of the fuel as well as the bed material [Olofsson *et al.* 2002] which could have detrimental effect on the melting properties of ash. High potassium in agricultural residues could be attributed to the use of fertilizers in agricultural farms [Amresto, 2002]. The study of potassium compounds in ashes is very important as the ash sintering and agglomeration can cause serious problems. Although ash content of coals is higher than biomass, many biomass ashes particularly those containing potassium have lower melting point than coal ashes which may cause bed sintering. Potassium is also found in coal but exists in the form of minerals and is harmless. However, sodium which is considered less important in biomass combustion may be troublesome during coal combustion [Leckner, 2011].

Use of biomass fuels alone or in combination with coal requires accurate prediction of the ash properties such as viscosity of the slags formed in ash and the temperature of the critical viscosity to control the ash and minimize slagging. Strength of ash fouling deposits is inversely proportional to the viscosity of the liquid phases present on them. The ash fractions derived from the co-combustion process melt at lower temperatures compared to ashes from coal combustion and have lower viscosity. Coal ash slags are complex blends of mainly aluminosilicates, silicates and oxides [Arvelakis, and Frandsen, 2007].

7.3 Causes of agglomeration:

Not only the type of the fuel and the presence of alkalis but also gas distribution, bed material size and nozzle types can also play an important role in agglomeration process. Agglomeration in fluidised beds is caused by improper plant control [Drift and Olsen, 1999] and involves a complex interplay of fuel, bed material and furnace operating conditions [Song Wu and Kumar, 1999]. Time scale of agglomeration process and maximum allowable temperature in the bed are strongly influenced by fluidisation conditions, temperature homogeneity, particles friction, gas atmosphere, bed and fuel particle size, combustion chemistry, system design and operational conditions [Drift and Olsen, 1999].

The main cause of the problem is the potassium contained in the fuel, retained in the ashes or partly released during the combustion process. Low ash content leads to high relative concentration of alkali in the ash indicating the possibility of agglomeration. Alkali silicates may be responsible for agglomeration at low bed temperatures. Only small portion of alkalis in the sand are in water soluble form or organically bound form, rest are in chemically stable form. Thus the sand is expected to be resistant to forming low melting temperature compounds [Song, *et al.* 1999].

Temperature is the most important parameter in bed agglomeration. Higher the temperature more severe the problems are [Drift and Olsen, 1999]. Temperature of burning fuel particles can be 100 – 200 °C higher than the average bed temperature and some of the materials can melt and initiate binding activities leading to agglomeration. Above a certain temperature minimum fluidisation velocity do not follow theoretical value but increases sharply with temperature. The temperature is called initial sintering temperature (Ts) [Gluckman *et al.* 1976]. It is an inherent property of particles and is governed by chemical composition and characteristics of particles [Lin *et al*, 2003]. Ts can be significantly lower than deformation temperature of ash [Compo *et al.*, 1987].

Higher the amount of fuel added to the bed, lower the agglomeration temperature. Thus accumulation of elements in the bed is responsible for the phenomena. Amount of fuel and ash fed to the system by a factor of three decreases agglomeration temperature by 25 °C [Drift and Olsen, 1999].

For silicate melts viscosity of the melt has to be taken into account. This will determine the fraction of the silicate required to cause stickiness and thus agglomeration. Around 20% of the molten material is enough to initiate bed agglomeration [Drift and Olsen, 1999]. The viscosity of the silica rich melts depends upon the ratio of acidic oxides (SiO_2, TiO_2 and Fe_2O_3) acting as network formers to the basic oxides (K_2O, Na_2O, CaO and MgO) acting as network modifiers. Alkali metals stabilize aluminium in the ash melt and reduce its tendency to act as a network modifier destroying the silica network and depolymerisation and melting at lower temperature. A reduced amount of alkali metals leads to an increased action of aluminium as a network modifier and results in lower melting as well as solidification temperatures of ash. At temperatures above 1300 °C, iron oxide is reduced to FeO and acts mainly as a network former leading to lower melting and solidification points [Arvelakis and Frandsen, 2007]. But this iron oxide reduction temperature is very much higher than the normal average operational temperature of fluidised bed combustors. However, there is a possibility that local temperatures (hot spots) may approach this limit and cause agglomeration.

In fluidised beds, when particle temperature is reached that of the bed, potassium is released partly in the form of gas (KCl or KOH). Dissociation of K_2CO_3 is greatly enhanced in the presence of water vapour and plays a role for the formation of KOH [Leckner, 2011]. The problems are more severe when high alkali content is combined with high sulphur (S), chlorine, silica and phosphorus [Drift and Olsen, 1999]. The importance of various potassium compounds including K_2SO_4 depends upon the availability of Cl and S in the fuel [Knudsen, *et al.* 2004]. The Cl and S form volatile compounds with potassium and their presence in the fuel determines the volatility of potassium. If Cl is low, K becomes less volatile and agglomeration problems are reduced [Drift and Olsen, 1999]. Presence of phosphorous contributes to the formation of low temperature eutectics with potassium, forming K_2PO_4 with Melting Point (MP) of approximately 800 °C [Zevenhoven 1999 – 2000]. Concentration of potassium below 2000 ppm (up to 4000 ppm in some cases is achieved without problems) is believed to be a safe limit for agglomeration. Carbonates decompose before they melt. Loss of carbonates therefore would not influence the melting behaviour [Drift and Olsen, 1999].

Bed agglomeration in fluidised bed combustors at temperatures of 760 – 900 °C is dominated by silica which may be the result of using silica or alumina-silicates as bed media [Thomas *et al.* 1995]. Ashes with low aluminosilicate and high alkali metal, calcium and sulphur content have the lower melting points. Ashes with medium to high aluminosilicate content melt at higher temperatures [Arvelakis and Frandsen, 2007]. Melting point of sand is 1450 °C [Werther *et al.* 2000]. Blend of Na_2O and SiO_2 can have a melting point of below 800 °C, and eutectics of $NaO.SiO_2$ and Na_2SO_4 can have melting point as low as 635 °C [Song Wu and Kumar, 1999]. The melting point of eutectic blend of 35% K_2O in K_2O-SiO_2 is as low as 770 °C, that of 32% K_2O in K_2O–SiO_2 is 769 °C [Thomas *et al.* 1995] and that of K_2O–CaO–SiO_2 [Lin and Dam-Johansen, 1999], is as low as 740 °C [Nielsen *et al.* 2000] which is also lower than typical fluidised bed combustion temperatures of 800 – 850 °C. Foster Wheeler's Karhula R&D centre indicated that salty ashes start to agglomerate at temperature as low as 600 °C [Song, *et al.* 1999]. Melting points of some of the mineral compounds found in ash are given in Table 7.1.

Table 7.1: Melting points of some minerals [Song and Kumar, 1999; Bryers, 1994]

Group	Mineral	Melting point °C	Group	Mineral	Melting point °C
Chlorides	NaCl	801	Sulphates	Na_2SO_4	882
	$CaCl_2$	782		K_2SO_4	1069
	KCl	770		$CaSO_4$	750 – 950
	$MgCl_2$	714		$MgSO_4$	1124 Decomp.
	$FeCl_3$	306		$Fe(SO_4)_3$	480 Decomp.
Carbonates	Na_2CO_3	851	Hydroxides	Na(OH)	318
	$CaCO_3$	1339		$Ca(OH)_2$	580 – H_2O
	K_2CO_3	891		KOH	360
	$MgCO_3$	Decomp. 350		Mg(OH)	350 – H_2O
	$FeCO_3$	Decomp. 350			
Phosphates	$Ca_2P_2O_7$	1230	Sulphides	Na_2S	1180
	K_3PO_4	1340		K_2S	470
	$Mg_3(PO_4)_2$	1184		FeS_2	1171

7.4 Agglomeration Mechanisms:

Different mechanisms for particle to particle attachment due to ash sintering and thus agglomeration have been proposed by researchers depending upon the type of interactions between the bed and fuel particles and their melting behaviour [Skrifvars, 1994]. One of the mechanisms of agglomeration is partial melting of low melting ash components to form a liquid phase of low viscosity which in turn forms necks between the bed particles. Lin, (2003) proposed that in a silicate system, elevated temperatures make eutectics of silica and alkalis to form a highly viscous and sticky liquid phase. In these systems "viscous flow sintering mechanism" also termed as "liquid phase mechanism" is a dominant mechanism. It is also possible that silicates and alumina-silicates melt of high viscosity form a layer on the surface of the bed material. The viscous liquid phase can also flow to form necks between the ash and bed particles.

Song and Kumar, (1999) have found two types of agglomeration. In the first case, interstices between the bed particles are filled with molten material that bonds the particles together, although individual particles are still distinguishable and have not undergone melting. In the second case the bed material had undergone complete melting. The both of these types are also described by Fin *et al* (1997) by burning straw in a fluidised bed combustor. Song, *et al.* (1999) proposed another mechanism for wood burning which is temperature driven rather than alkalis. They stated that fibrous structure of wood traps bed particles while burning. As burning structure temperature might be around 100 – 200 °C higher than the bed temperature these particles are partially melted and form agglomerate. Some of the other fuel ash constituents iron, S and calcium also get trapped in the clinker and it was thought alkali compounds may have been evaporated due to high temperature. Another type of agglomeration described by Fryda *et al.* (2006) is that in some cases, material do not chemically bond together due to ash melt but forms loose agglomerates, termed as conglomerates.

There is also a possibility of occurrence of chemical reactions on the surface of bed particles. Reaction of Lime with SO_2 to form $CaSO_4$ is thought to be responsible for the sintering of bed particles in fluidised bed combustors firing high Ca biomass materials [Skrifvars *et al.*, 1996].

Reactions of SiO_2 with alkali vapours and Ca may take place with soda lime glass formation [Leckner, 2011] by the following reactions.

$$SiO_2 (s) + 2KCl (g) + H_2O (g) \rightarrow K_2SiO_3 (l) + 2HCl (g) \quad (7.1)$$

$$SiO_2 (s) + 2KOH (g) \rightarrow K_2SO_3 (l) + H_2O (g) \quad (7.2)$$

$$CaO (s) + 2HCl (g) \rightarrow CaCl_2 (l) + H_2O (g) \quad (7.3)$$

$$SiO_2 (s) + 2CaCl_2 (l) + H_2O (g) \rightarrow CaSiO_3 (s) + 2HCl (g) \quad (7.4)$$

The products of this reaction have low melting point. The behaviour is observed with silica beds fired with biomass having high K and Ca but low Si. For high Si biomass in conjunction with K, agglomerates may form through molten ash particles and reaction layers on the bed particle surface as in the above case play a less critical role [Brus *et al.* 2005]. Alkali oxides can combine with Si compounds to form eutectic blends as shown in the following reaction.

$$SiO_2 + K_2CO_3 \rightarrow K_2O.SiO_2 + CO_2 \quad (7.5)$$

Presence of Fe_2O_3 reduces the agglomeration tendency as it may react preferentially with alkali compounds in the bed by the following equations forming blend with higher melting points in excess of 1135 °C [Armesto *et al.* 2002]. Iron in biomass indicates a greater extent of ion exchangeable material than is common in coal. Ferrous iron incorporated in silicates leads to lower melting points than ferric iron [Thomas *et al.* 1995].

$$Fe_2O_3 + K_2O \rightarrow K_2Fe_2O_4 \quad (7.6)$$

$$Fe_2O_3 + K_2CO_3 \rightarrow K_2Fe_2O_4 + CO_2 \quad (7.7)$$

7.5 Fate of Inorganic Elements during Combustion:

During fluidised bed combustion volatilisation of alkali metals and ash fusibility tend to be significantly lower than grate combustion systems which are operated at much higher temperature and ash is exposed to high temperature for a longer time. Inorganic constituents of biomass ash as well as bed material may undergo thermal degradation within the furnace.

Ash fraction is often mixed with mineral impurities such as sand, stones and earth present in biomass and bed material.

In the combustion of biomass most abundant volatile element is potassium originating from inherent ash. Potassium in biomass exists in different forms e.g. ionic, organometallic and salts. In all biomass potassium is atomically dispersed. Over 90% of the potassium in clean (non-soiled) fuels occurs either in water soluble or ion exchangeable form [Thomas, *et al.* 1995]. Potassium in entrained ash is typically present as very stable mineral silicate compounds and does not vaporize. During combustion potassium may be released from the fuel in a number of ways. It may voalitilise with organics and may release as short-lived metallic K. If fuel contains chlorine potassium may appear as KCl. In the absence of chlorine it may appear as hydroxide, oxide, sulphate or carbonate. In the gas phase KCl or KOH can react with SO_2 or SO_3 at low temperatures to form potassium sulphate which can condense and deposit [Thomas *et al.* 1995].

Metals play very significant role in the rate of de-volatilisation. De-volatilisation proceeds faster if potassium is present on the particle. Presence of potassium gives greater catalytic effect during both de-volatilisation and char combustion. By burning as received willow and washed with demineralised water Jones *et al.* (2007) found that the metals that can be removed by water washing are either not active as char burnout catalyst or they do not survive through to char burn out stage and lost during de-volatilisation. Potassium is also of interest due to its role as a catalyst for pyrolysis. It increases the rate of decomposition, change in product distribution and reaction mechanism [Jones *et al.* 2007]. Potassium remaining in char acts as a catalyst giving increased rates and higher carbon burn-out conversions efficiencies [Jones *et al.* 2004].

Fixing of alkali metals in ash depends upon other minerals present [Jenkins *et al.* 1998]. By combusting switch grass at 1373 K, Dayton *et al.* (1995) found that major loss of alkali occurs during combustion of char. Form of alkali in the fuel, bed material chemistry and fuel ash composition are also important factors in determining the split of alkalis between vapour and solid phases. Song, *et al.* (1999) have found steady increase in Na and K concentrations in the bed ash. Alkali retention rates were determined to be 12 – 43% and thought to be affected by operating conditions especially bed temperature. They found that alkali retention

was much less than those obtained by Tuncay *et al.* (1996) under similar conditions. Thus form of alkali in fuel is very important in predicting alkali retention. They found retention and accumulation of Na, K, and Ca. They also found that agglomerates have same alkali content as the bed material but there was much more sulphur, calcium, and iron (more abundant fuel ash) in agglomerates. The Ca and Mg, found in deposits on the outer surface of the bed particles, tend to adhere to the outer surface of the bed material.

Alkali metals are released at two characteristic temperature intervals 453 – 773K (180 – 500 °C) and > 773 K (> 500 °C) [Olsson *et al.* 1997]. First is associated with of organic phase and coincides with onset of pyrolysis. Second is due to alkali metal evolution from the ash component of char. Organic potassium evolves at the same rate as pyrolysis of biomass components and inorganic potassium vaporises as KCl and KOH through molecular diffusion [Yu *et al.* 2001]. According to Westberg *et al.* (2003) presence of KOH and HCl in gas phase increases the possibility of formation of KCl. Chlorine plays a critical role in the transformation of inorganic materials during combustion and has a significant tendency to vaporise potassium. Chlorine reacts with alkalis to form relatively stable and volatile alkali chlorides. Thus it is the concentration of chlorine rather than alkali which determined the extent of vaporisation. Stable chlorine containing vapours generated during combustion are alkali chlorides and hydrogen chlorides. Chlorine is one of the few materials that react with alkali in the form of silicate which are stable and volatile [Thomas *et al.* 1995]. Chlorine vaporizes almost completely during combustion forming HCl, Cl_2 and alkali chlorides. In fuels having low chlorine content alkali in the gas phase is present as hydroxide [Dayton *et al.* 1996].

According to chemical equilibrium calculations vaporized potassium is mainly present as gaseous KCl or KOH at high temperatures in the flue gas. As the temperature decreases the chloride and hydroxide are converted to sulphate by homogeneous gas phase reactions. Gaseous K_2SO_4 has a very low vapour pressure and becomes supersaturated as soon as it is formed forming new primary particles by homogeneous nucleation in huge numbers. However according to gas phase kinetics the formation of K_2SO_4 does not always follow equilibrium and only a part of the potassium in gas phase in converted [Christensen, 1995]. Equilibrium calculations for wood combustion have shown that main potassium containing

species formed at >1100 K (827 °C) are KCl, K_2SO_4 and KOH. While in the case of straw main species formed are $K_2Si_4O_9$, KCl and KOH [Wei *et al.* 2005].

The part of the gaseous potassium that does not form sulphates will either nucleate as KCl or K_2CO_3 or condensate or pre-existing particles at significantly lower temperatures than K_2SO_4. As time proceeds solid KCl or K_2CO_3 on the particles may undergo heterogeneous reactions with SO_2 (g) and form solid K_2SO_4. Fryda *et al*, (2006) also found layer on the sand particle due to SO_3 and CaO possibly due to sulphur caption on ash material.
Sulphur in all its forms quantitatively oxidises during combustion and some of it reacts with alkalis to form sulphates which are unstable at typical fluidised bed temperatures of around 900 °C. These sulphates can form agglomerates by mixing with fine ash [Thomas *et al.* 1995].

7.6 Agglomeration tendencies:

Agglomeration tendencies of different fuels are different depending upon the type and amount of alkalis present as well as the type of compounds formed during combustion. Rice husk, for example, contains 5.4% potassium as K_2O [Armesto *et al.*2002] and has considerable potential to cause agglomeration due to its high alkali content. Relative amounts of different compounds present in different fuels determine their agglomeration risk during fluidised bed combustion. Different measures e.g. alkali index, base to acid ratio (B/A), agglomeration indicator (AI), slagging potential etc. are used to determine the agglomeration characteristics of fuels, or combination of fuels in the case of co-combustion.

Alkali index (A) is the ratio of the sum of K_2O and Na_2O to higher heating value of the fuel [Drift and Olsen, 1999].

$$\text{AlkaliIndex} = \frac{K2O+Na2O}{HHV} \tag{7.8}$$

Values of alkali index higher than 0.17 kg/GJ are considered to cause possible problems. Values exceeding 0.34 kg/GJ almost certainly cause agglomeration and slagging problems.
Another alkali index represented by "I" is mass ratio of alkaline earth oxides to the alkaline oxides [Fernandez *et al.*, 2005].

$$I = \frac{CaO+MgO}{K2O+Na2O} \quad (7.9)$$

The "I" values higher than about 2 should not present risk of sintering.
Another measure used to assess agglomeration tendency of the fuel is the ratio of basic oxides to acidic oxides and is represented by "B" [Sakawa *et al*, 1982].

$$B/A = \frac{Fe2O3+CaO+MgO+Na2O+K2O}{SiO2+Al2O3+TiO2} * Ash\% \quad (7.10)$$

It indicates fusion characteristics and slagging potential of fuel ash. Values between 0.4 and 0.7 present low ash fusion temperatures thus a higher slagging potential.

Sulphur and chlorine make volatile compounds with K, thus presence of these elements also need to be considered in order to get an idea of the fate of potassium in the fuel during combustion process. Another agglomeration determination parameter which includes S and Cl known as agglomeration indicator AI [Vander Drift and Olsen, 1999] is defined as:

$$AI = \frac{Na+K}{2S+Cl} \quad (7.11)$$

The AI assumes that all the S and Cl in fuel react with the fuel alkali species. If AI > 1, alkali induced agglomeration is possible.

Bed agglomeration indices generally succeeded in predicting ash behaviour, especially taking into account S and Cl which facilitate alkali transfer to vapour phase. However, estimates based on these indices are not always accurate as the interactions of ash with bed material are not taken into account, therefore individual fuels and their blends should be tested for their agglomeration and sintering tendencies for the conditions of actual operation [Fryda *et al*, 2006].

7.7 Agglomeration control:

Agglomeration can be controlled by process optimisation, using additives and bed management. To avoid ash sintering and agglomeration problems combustor design and operation are very important. Agglomeration formation is often associated with the formation

of fuel rich hot spots in the bed. Thus, control of bed temperature and fuel distribution are the key parameters to control the operation of fluidised bed combustors.

For given operating conditions and feedstock composition, accumulation of alkali in the bed can be controlled by replacing adequate amount of bed material with fresh sand. Song, *et al.* (1999) observed that at higher bed material drainage rate and moderate bed temperature, agglomeration problems can be overcome. In full scale practice bed material is replaced before a critical ash accumulation or agglomeration level is reached. Thus operating conditions should be chosen to reduce sintering and agglomeration [Armesto, *et al.*, 2002]. It is also suggested to use alternative bed materials such as Alumina (Al_2O_3) and Mullite ($Al_2O_3.SiO_2$) if fuel used is an agglomeration risk [Drift and Olsen, 1999]. Ferric oxide can sustain long term operation and thus can be used instead of silica sand [Grubor, *et al*, 1995].

Silica used as a bed material forms low melting eutectic blends with alkali compounds present in biomass [Drift and Olsen, 1999]. The addition of Ca and Kaolin $Al_4Si_4O_{10}(OH)_8$) in eutectic formed by high alkali ash fuels in quartz sand bed is a proven mechanism to control and prevent agglomeration [Ohman and Nordin, 2003; Risnes *et al*, 2003; Ohman and Nordin, 2000; Steenari and Lindquist, 1998; Leckner, 2011]. Olofsson *et al.* (2002) used additives mullite, calcite, clay and a blend of clay and calcite, (10% w/w), for capturing alkali. Some of the alkali getters described in literature are given in Table 7.2.

Table 7.2: Alkali getters [Van Der Drift and Olsen,1999]

Compound	Formula	Action
Kaolin	$Al_2SiO_5(OH)_4$	chemical getter of alkalis, binds alkali metals into harmless components
Magnesite	MgO	influences the viscosity of the melt
Gibbsite	$Al(OH)_3$	decomposes to very porous Al_2O_3 capable of gettering alkalis physically
Dolomite	$MgCO_3.CaCO_3$	cheap and proven to reduce agglomeration in straw combustion

Ohman *et al.* (2003) found that agglomeration temperature with MBM alone was 805 °C. With the addition of RDF (2/3 on energy basis) it went up to 830 °C. Addition of 5% dolomite to MBM/RDF blend took the agglomeration temperature to 860 – 890 °C while the addition of 5% kaolin resulted in agglomeration at 905 °C. They concluded that MBM combustion in fluidised beds of quartz is expected to be problematic and addition of kaolin and possibly dolomite could reduce the risk to moderate levels. Co-combustion and addition of sewage sludge could be cheaper options to control bed agglomeration. Addition of sewage sludge with high Al and Si content removes fine potassium containing particles possibly by the following reaction.

$$2KCl\ (g) + Al_2O_3.2SiO_2\ (s) + H_2O\ (g) \rightarrow K_2O.Al_2O_3.2SO_2\ (s) + 2HCl\ (g) \quad (7.12)$$

Co-combustion with suitable fuels (having low Cl content) can also reduce or even avoid the problem [Leckner, 2011]. Blending of straw with wood and coal is also successful to some extent.

Al and Ca [Ohman and Nordin, 2003] interacts with the low melting K and Na containing silicates shifting their melting temperature to higher values (>1000 °C) thus provide remedy against severe agglomeration [Fryda *et al.* 2006]. If sintering is caused by alkali silicates, finely divided metal oxides such as CaO, Fe_2O_3 or Al_2O_3 can be added to react with Alkali silicates to raise melting points [Wall *et al.* 1975; Tamhankar and Wen, 1981]. Clay ($Al_2O_3.2SiO_2.2H_2O$) is found to be effective in increasing melting point of alkali silicates by forming alkali aluminium silicates [Song Wu and Kumar, 1999].

$$Al_2O_3.2SiO_2 + 2NaCl + H_2O \rightarrow 2HCl + Na_2O.Al_2O_3.2SiO_2 \quad (7.13)$$

If fluidisation velocities are several times higher than minimum fluidising velocity, bed particle agglomeration does not cause complete de-fluidisation at an early stage [Kunii and Levenspiel, 1991]. Thus 2 – 3 grain agglomeration in the early stage would not cause de-fluidisation directly [Fryda *et al*, 2006].

Fryda *et al.* (2006) have shown that bed particles were coated with a 10μm layer of ash deposition due to melting of Na and K silicates but the layer did not grow to problematic diameter. High Al content of the coal ash prevented the layer from growing further. As they

used very high fluidisation velocities in comparison to the minimum, attrition of the particles may have also prevented growth of the layer.

7.8 Co-Combustion and Agglomeration:

Co-combustion could help reduce or prevent agglomeration problems. Combination of fuels in such a way that presence of compounds result in increasing the time before agglomeration occurs. It is understood that biomass fuels are more likely to cause agglomeration during combustion in fluidised beds as compared to coal. Therefore it is a very risky business to burn biomass fuels on theirown. In order to reduce their agglomeration potential it is possibly better to combust them with coal in certain proportions. It may be possible to blend different biomass so that their net agglomeration tendency is lower.

However, in some combinations agglomeration problems become worse due to different characteristics of the combined fuels. Severe agglomeration was observed by Fryda *et al.* (2006) during MBM and olive bagasse co-combustion, due to the absence of coal mineral matter. Coal ash is composed of mineralogical material while biomass ash is largely ionically bound to the organic matrix and as distinct minerals and very fine salt particles [Ansen, 1998]. The inert clay mineral matter of coal acts as a remedy to moderate alkali ash content of MBM. Fryda *et al.* also found that ash Ca content in the blend was not capable of inhibiting the formation of eutectics due to the presence of K, Na and P in the blend ash. In the co-combustion of olive bagasse and MBM, combined alkali content is higher than what it should be if coal is used instead of olive bagasse. Moreover, higher portion of lower viscosity alkali melt quickly covers the bed particle increasing agglomeration potential.

So far in this chapter literature reviewed on agglomeration is presented. In the following paragraphs pre-testing and testing of different fuels for their agglomeration tendency is presented.

7.9 Pretesting of Fuels for Agglomeration:

Prior to performing bed agglomeration tests in the test rig, agglomeration potential of biomass materials used in the tests has been calculated and muffle furnace tests have been

performed to assess their behaviour towards agglomeration during combustion in fluidised bed.

7.9.1 Agglomeration potential calculations:

It is well known that biomass materials cause agglomeration when fired in a fluidised bed due the presence of alkali metals particularly potassium. Agglomeration indices are usually used in order to pre-assess the behaviour of biomass materials during combustion in a fluidised bed. Therefore, the agglomeration potentials of the biomass fuels using agglomeration indices available in literature have been calculated using the data provided by British Sugar. The results of the calculations are given in Table 7.3. Due to lack of data availability some assumptions has been made in calculating the results.

- Sodium oxide (Na_2O), for all the materials, is calculated from Na assuming that all the Na exists as Na_2O
- Chlorine is assumed to be zero in all the three biomass fuels as no clear information about its presence is available
- For pressed pulp, all the oxides are calculated from elemental analysis assuming that all the individual elements exist as their oxides and magnesium (Mg) is assumed to be zero as no information is available about its presence

The table shows that Alkali index "A" for raffinate and vinasse is very high showing that there are considerable chances of agglomeration during firing of these fuels. The "A" value for PP is low but still more than 10 times above the safe limit of 0.17 kg/GJ. Alkali index "I" for vinasse (0.0035) and raffinate (0.008) is considerably lower than safe limit of above 2, indicating higher chances of sintering. However, for PP the "I" value is very close to safe limit. Agglomeration indicator "AI" for vinasse and raffinate is about twice the safe limit of below 1, while for PP it is very very low. The above discussion indicates that, within the margin of assumptions made, there is very high potential of agglomeration during raffinate and vinasse combustion than that for pressed pulp with raffinate presenting the worst case.

Table 7.3: Predicted Agglomeration potentials of Sugar Co-Products

	Raffinate	Vinnase	Pressed Pulp
Na_2O (%)	2.12	1.81	0.135
K_2O (%)	6.597	2.243	1.8
MgO (%)	0.008	0.007	0
CaO (%)	0.062	0.007	1.68
K (%)	3.92	2.67	0.75
Na (%)	1.57	1.34	0.1
S (%)	0.78	0.96	0.25
HHV (MJ/kg)	6.7	6.41	5.3
Alkali index "A" (kg/GJ)	13	6.3	1.9
Alkali index "I"	0.008	0.0035	1.62
Agglomeration indicator "AI"	2.14	1.92	0.11

7.9.2 Muffle furnace tests:

Above discussion shows that vinasse and raffinate both possess very high agglomeration tendency. Therefore, prior to combustion tests, it was decided to perform controlled tests of different blends of vinasse and raffinate with sand in a muffle furnace. During these tests vinasse and raffinate were mixed with sand in different ratios and kept at a controlled set temperature for a specific period of time. The results of muffle furnace tests are summarised here. Details of the tests are given in Appendix D.

In the first set of tests percentage of vinasse in sand was varied from zero to 50% to make total sample weight for each test equal to 40 g. The samples were kept at 800 °C in muffle furnace for 60 minutes. The observations made after each test are given in Table 7.4. It can be observed form the table that during each test considerable weight of the sample was lost. Careful attention reveals that almost all the vinasse sample evaporated during the tests. Observations show that the surface of the sample was found to be hard when hot but loosened as it cooled down. There was no clinker found in the test samples when tested at 800 °C,

therefore, the test temperature was increased to 850 °C in the subsequent tests. Observations show that there was no clinker found when vinasse content in the sample was increased up to 20%. When vinasse content was increased beyond 20%, sample started ignition. First signs of clinker were found at 30% vinasse in the sample but the clinker was easily breakable which was the case even when vinasse content was increased to 75%. However, as can be noted from the table most of the sample was lost as crucible broke down.

In the above tests fresh sand was used each time. Agglomerates formed during the tests were easily separable even at 75% vinasse content in the sample. In order to simulate continuous combustion operation, in the subsequent tests it was decided to perform top up tests, where weighed amount of vinasse was added to the sample left in the previous test. The sample was kept in muffle furnace controlled at 850 °C for 20 minutes during each top up test. Amount of vinasse added, to 30 g sand, for each top up was 12 g, which is equivalent to around 30% vinasse content in the sample, see Table 7.5. Increased amount of clinker was observed during subsequent tests due to accumulative effect. After top up test number 7, hard agglomerates were observed. At this point total test time was 2 hours and 20 minutes and total amount of vinasse added was 84g. Thus total amount of vinasse added to the sand was around 74%. However, this situation was not observed in the previous test with fresh sand used in each test even when sample contained 75% vinasse. This indicates that accumulative effect of vinasse top up and prolonged test time resulted in the formation of hard agglomerates. It can be concluded that soft agglomerates found during first few top up tests were hardened as more vinasse was added and subjected to high temperature for prolonged period. The agglomerates also grew in size as the tests progressed and eventually after top up test number 10 (3 hours and 20 minutes, 80% vinasse), all the material turned into a bigger, hardened lump.

Table 7.4: Muffle furnace tests with Vinasse-Sand blend (time = 60 minutes)

Biomass/Sand (%)/(%)	Temperature (°C)	Weight loss (%)	Observations
0/100	800	0.85	Sand has been discoloured to mostly red
20/80	800	19.83	The surface was hard seconds after being taken out from the furnace but can easily be separated even still hot. Mostly un-clinkered when cooled down to room temperature
30/70	800	29.31	Not much different to the 20%/80% blend. Surface was hard when still hot but can be easily separated when cooled down to room temperature
50/50	800	47.82	Surface was hard when still hot. Mostly un-clinkered but some clinkers became harder & unbreakable even cooled down to room temperature
0/100	850	1.15	Sand has been discoloured to mostly red.
8/92	850	8.75	It was extremely easy to separate when cooled down to room temperature
10/90	850	10.43	No clinker was found although sample hardness was not tested when still hot
12/88	850	12.28	Surface was slightly rigid than the 8% Vinasses sample
14/86	850	14.29	Mostly unclinkered when cooled down to room temperature.
16.7/83.3	850	16.67	The surface was hard seconds after being taken out from the furnace but mostly unclinkered when cooled down to room temperature
20/80	850	19.77	The surface was hard when just being removed from the furnace but mostly unclinkered when cooled down to room temperature

25/75	850	24.4	Sample was ignited when first put into the furnace. Surface was hard when just being removed from the furnace but mostly unclinkered after being cooled down to room temperature
30/70	850	29.13	Fire can be seen when first put into the furnace. Surface was hard when still hot and clinker can be noticed but can easily be separated when cooled down to room temperature
50/50	850	49.5	Fire was intense when first put into the furnace and overflow of Vinasse was observed. Surface was hard when still hot but can easily be separated when cooled down to room temperature
75/25	850	NA	Fire was intense when first put into the furnace and broke the crucible. Not much sample left but clinker was hardened when cooled down to room temperature but can still be separated.

Table 7.5: Top up Muffle furnace tests with Vinasse-Sand blend

Biomass/Sand (%)/(%)	Weight loss (%)	Observations
Temperature = 850 °C, Time for each top up = 20 minutes		
30/70 (Top-up 1)	29.23	Mostly un-clinkered when cooled down to room temperature.
30/70 (Top-up 2)	28.07	Surface became harder when still hot but can easily be separated when cooled down to room temperature.
30/70 (Top-up 3)	27.7	Sand has been discoloured to mostly dark grey
30/70 (Top-up 4)	27.34	Surface was hard seconds after being removed

		from the furnace. The amount of clinker began to form increased.
30/70 (Top-up 5)	26.92	Surface was harder when still hot but can still be separated. More clinkers can be seen after being cooled down to room temperature
30/70 (Top-up 6)	26.65	Sand can be separated with extra force after being cooled down to room temperature but more clinkers can be noticed
30/70 (Top-up 7)	26.23	Very difficult to separate when cooled down to room temperature. More clinkers were formed
30/70 (Top-up 8)	25.75	Very hard to separate the sample even with considerable force. Clinkers were getting bigger
30/70 (Top-up 9)	25.5	Extremely difficult to separate the sample even after being cooled down to room temperature.
30/70 (Top-up 10)	25.2	Large lump of clinker was eventually form and extremely hard to separate even after being cooled down to room temperature

In order to assess the effect of alkali content on agglomeration, further test were carried out in muffle furnace with raffinate. Rafinate has higher alkali content as compared to vinasse.

During these tests raffinate was mixed with sand up to 50% in sample weighing approximately 40 g. The samples were kept in muffle furnace for 60 minutes at 850 °C. Conditions of the tests and observations made are given in Table 7.6. It can be observed from the table that weight of the sample lost during these tests was less than those performed with vinasse which indicates that more portion of raffinate was left in the sample as compared to vinasse. The results show that after each test the sand became harder to separate as raffinate content in the sample was increased. The sand turned into an unbreakable lump when raffinate content in the sample was increased to 50%. This condition was not observed with vinasse even with 75% vinasse in the sample where agglomerates were separable by hand which indicates that amount of alkali in the fuel influences agglomeration conditions.

Therefore, not only the time of test but the amount of alkali in the fuel affects agglomeration phenomena. The results of these tests agree with the results of calculations using agglomeration indices in the above section and prove that agglomeration indices are good indicators of agglomeration potential and should be used to pre-assess the behaviour of potential fuels before feeding into fluidised bed.

Table 7.6: Muffle furnace tests with Raffinate-Sand blends

Biomass/Sand (%)/(%)	Weight loss (%)	Observations
Temperature = 850 °C, Time = 60 minutes		
7/93	6.6	Sand has been discoloured to white and grey. Surface was slightly hard when hot but can easily be separated when cooled down to room temperature
14/86	12.54	Sand has been discoloured to white and grey. Surface was hard when still hot. After being cooled down to room temperature, extra force was needed to separate the sample
25/75	21.9	Surface was extremely hard when still hot. Extra force was applied to separate the sample after being cooled down to room temperature
50/50	43.99	Surface was extremely hard and unbreakable even cooled down to room temperature. No change at all of re-fluidisation

7.10 Agglomeration tests in Fluidised bed:

Agglomeration indices calculations and muffle furnace tests proved that vinasse and raffinate could be problematic when fed into the fluidised bed. However, solid biomass such as pressed sugar beet pulp and wood may be less problematic due to their lower alkali content. Therefore, longer term co-firing tests with coal and pulp 50/50 blend were undertaken in the current project and scanning electron microscopy (SEM) was employed to determine quantitatively the "pick up" of alkali metals by the bed materials, details of the analysis are

given in Appendix E. No problems of bed agglomeration were observed during the extensive tests with coal or with coal-wood pellets or coal-wood chips so that the investigation of bed "pick up", and hence potential bed clinkering, concentrated mainly on co-firing of coal and pressed sugar beet pulp.

However a previous test in which raffinate was co-fired with coal on the full scale fluidised bed hot gas generator at British Sugar's Cantley factory had indicated that agglomeration occurred relatively rapidly under the conditions of the test. To confirm this result, tests were undertaken on the pilot scale facility in which vinasse and raffinate were co-fired with coal. The raffinate was also co-fired with natural gas to assess the influence of coal ash on bed agglomeration.

7.10.1 Coal Raffinate Co-Firing:

Thoresby singles coal and raffinate both provided by British Sugar were used in the tests. Raffinate is similar to molasses in appearance (dark brown) and is fairly sticky, slightly viscous liquid material. It has a viscosity of 150 mpa.s (0.15 kg/m.s) and density of 1320 kg/m^3. The coal supplied by British Sugar was 5 – 8 cm and was crushed and sieved to get 6 – 10 mm size used for the tests.

The fluidised bed was fired with natural gas in order to raise the bed temperature. Bed temperature was raised to 600 °C before coal feeding was started to make sure that the bed temperature was well above the auto-ignition temperature of the coal. After getting stable conditions with coal, raffinate feeding was started. Time for which coal only was fed into the bed was approximately 50.5 minutes (0.84 hrs). Total time for gas burning and coal feeding until the start of raffinate feeding was around 85 minutes (1.42 hrs).

The resultant bed and freeboard temperatures 0.24 m above the static bed together with the pressure drop across the bed during this test are presented against time in Figure 7.1. The conditions of the test are given in Table 7.7.

Approximately 40 minutes after the start of co-firing the pressure drop experienced a sharp fall which was associated with the onset of agglomeration and partial de-fluidisation of the

bed. Under these latter conditions, the pressure drop is no longer associated with supporting the mass of the suspended bed particles and hence falls to a value of that for a partially "packed" bed. The phenomena of bed agglomeration results in temperature gradients in the bed and according to Armesto *et al.* (2002) large fluctuations in the bed pressure are first signs of onset of agglomeration. In Drift and Olsen, (1999) view point, upon onset of agglomeration, temperatures within the bed start to deviate.

Subsequent inspection of the bed indicated a substantial volume of agglomerated sand particles therefore confirming that the pilot scale rig behaves in a similar fashion to the full size plant at Cantley where considerable bed clinkering was observed after 1.95 tonnes of raffinate was added to 40 MW fluidised bed (used as a hot gas generator) maintained at 850 °C at an average flow rate of 0.42 m^3/h (0.56 tph) with a maximum flow of 0.8 m^3/h (1.07 tph) for 3.5 hours [Roskams, 2006]. Once the bed began to clinker, the fuel feed, but not the fluidising air, was switched off so that the bed temperature decreased. The subsequent recovery in bed pressure as shown in the figure is probably due to solidification of the sticky deposits and partial breakup of the weak brittle bonds between sand particles by the air.

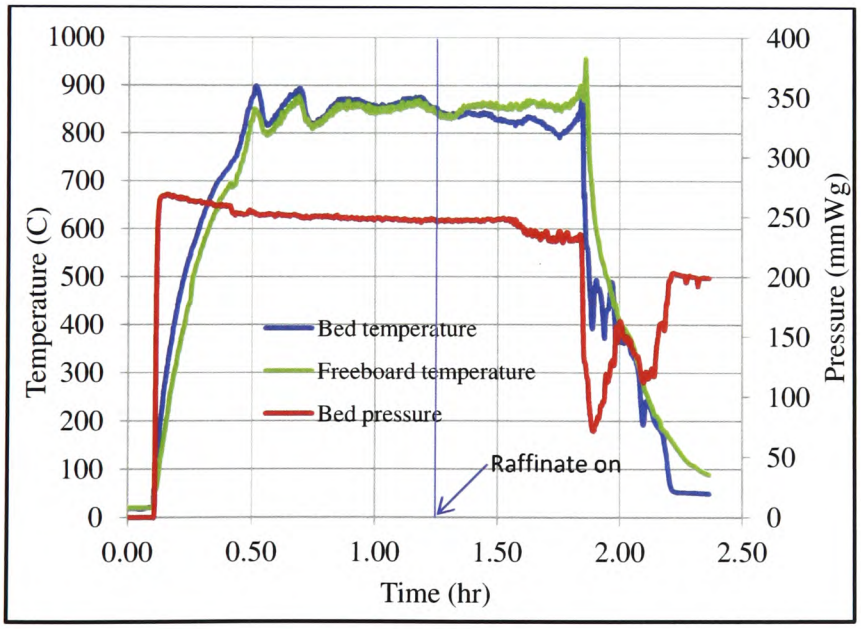


Figure 7.1: Bed behaviour during co-combustion of coal and raffinate

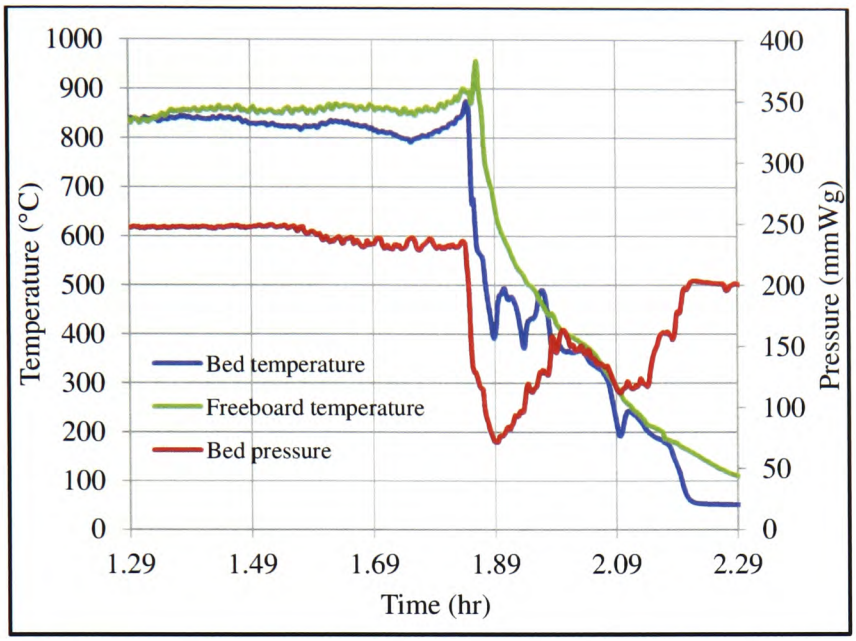


Figure 7.2: Temperature and pressure fluctuations during agglomeration test of co-combustion of coal and raffinate

It was realised that after around 10 minutes (0.17 hrs) of raffinate feeding, thta the bed temperature (BT) started declining from 840 °C so as the bed pressure (BP) started going down slowly from 240 mmWg. Bed pressure is a function of bed depth. It also depends upon fluidising velocity (gas flow and bed temperature). After approximately 29 minutes of raffinate feeding into the bed it was noted that bed temperature dropped down to 800 °C and bed pressure dropped down to 230 mmWg. At this point, as there was not a huge change in the bed pressure, it was thought that the high moisture content of raffinate rather than agglomeration might be responsible for the declining of the bed temperature. Decline in bed pressure, at that moment, was thought to be due to decrease in bed temperature. It was decided to increase the coal feed flow from 2.8 kg/h to 3.2 kg/h (next calibrated setting on the control) to increase the bed temperature. However, it is possible that something had started happening already in the bed as will be explained later.

Table 7.7: Test conditions for Coal-Raffinate test

Coal flow for 81 min (kg/h)	2.8
Coal flow for 81 min (kW)	23.3
Coal flow for 7 min (kg/h)	3.2
Coal flow for 7 min (kW)	26.7
Raffinate flow (l/h)	2.88
Raffinate flow (kg/h), Density = 1320 kg/m^3	3.8
Coal to Raffinate feed ratio (kg/h)/(kg/h)	0.84
Coal (%)	45.7
Raffinate (%)	54.3
Coal only feed time (hrs)	0.9
(Coal + Raffinate) feed time (hrs)	0.57
Total coal feed time (hrs)	1.47
Total coal feed (kg)	4.22
Total reffinate feed (kg)	2.2
Coal to raffinate mass ratio (kg/kg)*	1.92
Sand to raffinate ratio (kg/kg)*	3.4

*Ratio of total material fed to the bed

It should be noted that soon after raffinate was fed onto the bed, freeboard temperature became higher than BT, see Figure 7.2 which shows a magnified view of the changes happening during early stages of agglomeration and afterwards. The rise in freeboard temperature was observed to be around 50 °C with a peak value of around 100 °C just before raffinate feed was switched off. This observation is in line with the full scale raffinate trials at British Sugar's Cantley site where freeboard temperature (downstream in Bull ring) was observed to rise by around 50 °C [Roskams, 2006]. It is evident from the figure that agglomeration and complete de-fluidisation are preceded by changes in temperatures and pressures in and across the bed. It is also clear that a considerable proportion of the raffinate was burning above the bed resulting in higher freeboard temperature.

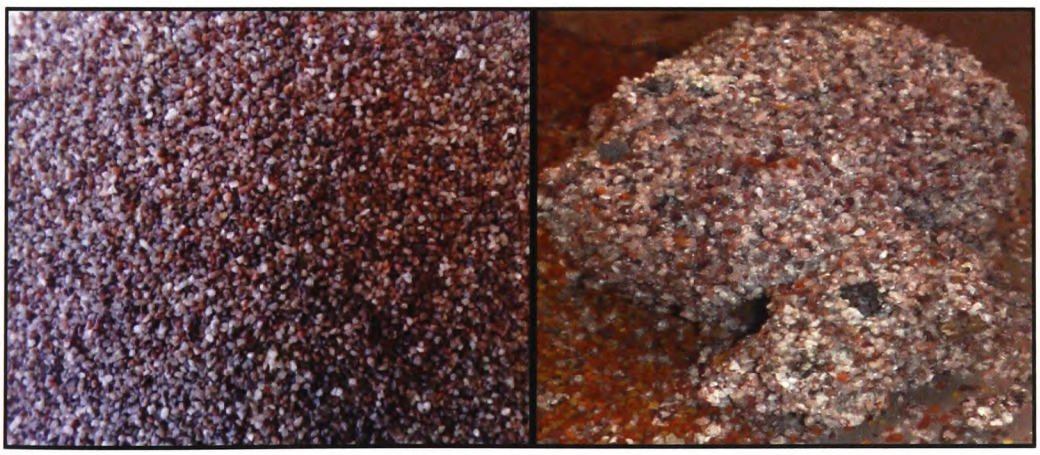
As the coal flow was increased BT started going up, so as the FBT_1. BP fluctuated between 230 – 235 mmWg. Within 6 minutes of increase in coal flow BT went up to 850 °C and FBT_1 up to 900 °C. At this point there was a sudden increase in the BT which went up to 874 °C. Immediately after this, both BT and BP started declining sharply, an indication of agglomeration and bed slump (sudden loss of fluidisation). Both raffinate and coal feeds were stopped but air fan was kept running to make sure that all the fuel in the bed was combusted.

From the figure 7.2 it can be seen that after switching off the fuel feed there are two peaks in bed temperature when it dropped down to 400 °C and another peak when BT went down to 200 °C. Agglomeration can cause local high temperatures. As there was only one temperature measurement in the bed, it is not possible to find out the exact cause of peaks in bed temperatures. However the peaks can be attributed to the burning of un-combusted coal/char in the agglomerated bed material and to the inherent property of agglomeration to cause local high temperatures.

Also it can be seen that BP came down to around 65 mmWg and then went up. A closer look at the plot reveals that this peak in BP is coincident with the BT peaks, justifying the above said argument that as temperature came down agglomerated material started breaking down into individual particles and resulted in partial recovery of bed pressure. The bed pressure again came down with BT and then went up again, finally stabilising at 200 mmWg. The difference between initial BP of 240 mmWg and final BP of 200 mmWg could be due to the bed material used in the form the larger lump found in the bed and lesser material was available to be fluidised. The restoration of bed pressure indicates that agglomerated material broke down as bed temperature dropped due to air velocity and was fluidised again.

Bed temperature of 874 °C as observed during the last moments before bed slump could give a vital information about the behaviour of raffinate combustion in a fluidised bed. Burning coal char particles might have considerably higher temperature than the bed temperature measured by thermocouple. This higher particle temperatures or hot spots can initiate agglomeration phenomenon locally which then extends throughout the bed due to the fact that these agglomerates act as nuclei to attract other particles to form bigger agglomerates.

Post experiment bed examination showed that top of the bed was fluidisable. However, there was an evidence of the presence of white particles possibly coated with sticky material responsible for agglomeration and bed slump. The particles were also bigger than the original sand particles fed into the bed. At the bottom of the bed, just above the stand pipes, there was a big lump of the agglomerated bed material, see Figure 7.3. The lump was possibly formed on the top of the bed, close to the raffinate feed point, then settled down to the bottom of the bed i.e sand from the bottom had been blown to the top and eventually resulted in settling down the lump. There is also a possibility that stickiness of raffinate may have resulted in the formation of lump which then strengthened over time due to high temperature. At Cantley trails, it was concluded that the agglomeration could be due to accumulated effect of raffinate aver the run time and during these trials, sand to raffinate ratio was 6 before raffinate feed was stopped due to agglomeration. During present study the ratio was 3.4, see Table 7.7, which suggest that during current tests agglomeration occurred relatively quickly as compared to Cantley trials. There is also a possibility that higher fluidising velocity at Cantley trails, almost twice that in present study, may have prevented the bed from being agglomerated for relatively prolonged time which allowed more raffinate to be fed into the bed before agglomeration occurred. During present study bed slumped within 1 hour while at Cantley trials the bed fused after 3.5 hours of raffinate feeding which again supports above said argument of higher fluidising velocity being responsible for prolonged operational time.



(a) Top of the bed (b) Agglomerated lump

Figure 7.3: Bed material after Coal-Raffinate co-firing

The findings from the tests are in line with the muffle furnace test which indicated that agglomeration problem can occur during raffinate firing in fluidised bed. However, during muffle furnace tests agglomeration occurred with raffinate content of 50% (sand:raffinate = 1:1). During fluids bed test the ratio of sand to raffinate was 3.4 (22.5% raffinate in sand) which means that during fluidised bed tests agglomeration occurred with lower amount of raffinate as compared to muffle furnace tests. It was expected that fluidised bed agglomeration test should have been longer than muffle furnace due to following reasons.

- During fluidised bed combustion fluidisation phenomena caused by air or gas flowing from the bottom should, to some extent, result in increased amount of raffinate feed into the bed before occurrence of agglomeration
- Coal ash may also affect the agglomeration behaviour and may result in higher amount of raffinate being introduced into the bed before agglomeration occurred

In the fluidised bed test agglomeration occurred within 35 minutes of raffinate feeding but muffle furnace test was one hour long which indicates that agglomeration in the muffle furnace may have occurred earlier in the test. Muffle furnace test with 7% raffinate in sand has shown signs of agglomeration and harder agglomerates were found as raffinate percentage was increased. Therefore, it can be concluded that agglomeration during fluidised bed test may have started earlier which may have strengthened with time and eventually resulted in de-fluidisation of the bed. However, as above discussion indicates that muffle furnace results cannot be directly compared with fluidised bed tests due to different dynamic conditions but they can be used to pre-assess potential fuels.

Samples of the bed material, one from the top of the bed and one from the agglomerated lump, were analysed by SEM to check the possibility of the presence of alkalis responsible for the bed agglomeration. The results of SEM are given in Table 7.8 and SEM scan is shown in Figure 7.4. It can be seen from the table that surprisingly concentration of alkalis in the lump is considerably lower than that in the top of the bed. Thus, it can be thought that the lump was formed during the early stages of the raffinate feeding when BT and BP first started to fell down. Also it is possible that the lump became strengthened because of subjection to high temperature over a period of time and was unbreakable by the force of the air unlike the rest of the bed. As it is mentioned earlier that top of the bed was un-agglomerated. It can be

concluded that when BT came down, melted phase solidified and push of the air helped to break the loosely bonded lump particles down to individual particles.

Table 7.8: SEM results of Raffinate-Coal Combustion test

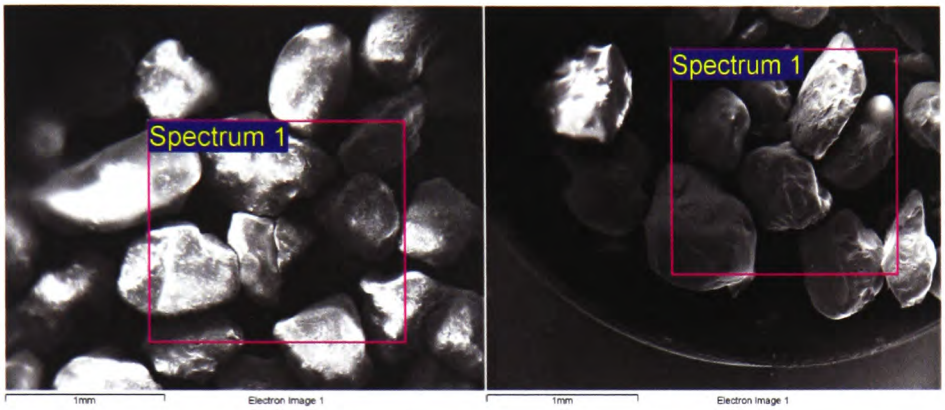
	Top of the bed		Agglomerated lump	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	30.88	43.48	38.42	49.93
O	36.76	38.86	38.44	37.51
F	0.72	0.64	0.55	0.46
Na	2.92	2.15	1.38	0.93
Mg	0.1	0.07	-	-
Al	0.7	0.44	0.26	0.15
Si	10.72	6.45	16.75	9.31
S	4.86	2.56	0.39	0.19
Cl	0.21	0.1	-	-
K	12.05	5.21	3.57	1.42
Ti	0.09	0.03	0.04	0.01
Ca	-	-	0.2	0.08

Also there were found some small lumps of agglomerated sand which were easily breakable by hand. The reason for these could be that they settled down onto the bed parts which were stagnant or un-fluidised and thus were not broken by the force of the air.

Softening temperature of the ash is thought to be the agglomeration occurrence temperature in fluidised beds. Ash fusion temperatures for coal used in the test are given in Table 7.9. The table shows that softening temperature of coal is above 1060 °C. However, during the test agglomeration occurred at a temperature of 874 °C. This shows the influence of alkalis present in the fuel and silica in the bed to form a composition which tends to reduce agglomeration temperature considerably.

Table 7.9: Ash fusion temperature of Thoresby coal under reducing atmosphere (50% CO_2 and 50% H_2) [BCURA website]

Deformation Temperature (°C)	1060
Hemisphere Temperature (°C)	1090
Flow Temperature (°C)	1220



(a) Top of bed (fluidisable) (b) Agglomerated lump

Figure 7.4: SEM scan of Coal-Raffinate test

The average content (by mass) of sodium and potassium in the outer layer of the particles removed from the bed after the test as measured by SEM analysis were 2.1% and 7.8% respectively. The high levels of potassium are associated with the formation of potassium silicate eutectics which can melt at temperatures as low as 760°C. The resultant molten, sticky silicate deposits on sand and ash particles appears to be the likely cause of agglomeration of the bed. The substantial "pick up" of potassium is not unexpected since raffinate typically contains very high levels (13.0%) of this metal, see Table 7.10. Similar observations were made by Lin *et al.* (1999) where they found during straw combustion that potassium was responsible for agglomeration as, during combustion, it transforms from organic to inorganic forms of low melting point K_2O-SiO_2.

Table 7.10: Alkali Metal Contents of Raffinate, Vinasse and Sugar Beet Pulp on dry basis [British Sugar]

	Sodium (Na) %	Potassium (K) %	Calcium (Ca) %
Raffinate	3.6	13.0	0.76
Vinasse	2.5	7.0	0.05
Pressed Pulp	0.1	0.75	1.2

Table 7.11: Flue gas analysis of Coal amd Raffinate Co-Firing test

	Coal only		Coal + Raffinate	
	Measured	Corrected to 6% O_2	Measured	Corrected to 6% O_2
O_2 (%)	14.3	6	11.4	6
CO_2 (%)	3.8	8.5	5.4	8.4
CO (ppm)	160	358	2845	4445
NO (ppm)	386	864	386.5	604
NO_2 (ppm)	1	2	0.6	1
NO_x (ppm)	387	866	387.1	605
SO_2 (ppm)	379.1	849	244.6	382
H_2 (ppm)	8.6	19	611	954

Emissions data given in Table 7.11 is taken as an average over a period of at least 10 minutes. For coal and raffinate co-firing, the emissions data is averaged over a period for which coal flow was the same as for "coal only" analysis in the above Table. It can be observed from the table that concentration of O_2 decreased while that of CO_2 increased after the introduction of raffinate marking the combustion of raffinate. Considerable increase in CO emissions was observed due to incomplete combustion. The presence of water in raffinate (almost 50% of raffinate flow) could have contributed to the conversion of CO to CO_2 by water gas shift reaction, given below [Twigg, 1989], as can be evidenced by the considerable increase in the concentration of H_2. The endothermic nature of the water gas shift reaction, alongside water, may have contributed towards bed temperature decrease in the early stages of raffinate introduction as can be observed in Figure 7.1.

$$H_2O + CO \rightarrow CO_2 + H_2 \Delta H^{\circ}_{298} = -41.1 \text{ kJ/mol} \quad [7.14]$$

The table shows that the emissions of NO_x remained unchanged after the introduction of raffinate. This may be explained on the basis that both the coal (1.62%) and raffinate (1.6%) contain almost the same nitrogen content on as received basis. However, emissions of SO_2 decreased after raffinate introduction which again explains the possibility of formation of H_2SO_4, as discussed in Chapter 6, by the reaction of SO_2 with water present in raffinate. However, during full scale tests at Cantley, emissions of NO_x and SO_2 incerased slightly [Roskams, 2006]. This could be due to the reason that at Cantley emissions were monitored downstream of the fluidised bed combustor while during present study they were measured just above the fluidised bed which means that gaseous reactions may have occurred beyond the measurement point and the data could have been different if measured further downstream.

7.10.2 Natural gas and Raffinate Co-Firing:

During previous test of co-combustion of coal with raffinate, agglomeration occurred very quickly possibly due to difficulty in properly controlling the bed temperature. So, it was decided to conduct controlled bed temperature test with raffinate and natural gas instead of coal as bed temperature can be better controlled with gas firing than coal firing. Also as the gas burner is firing into the combustion chamber (acting as plenum chamber) to the fluidised bed, flue gas coming from the distributor will be at a higher temperature as compared to air and thus will have a higher volumetric flow. This might exert a higher force that will break up the loose agglomerates and therefore agglomeration temperature might be higher than that achieved with raffinate coal co-firing.

After the coal-raffinate co-firing test bed was replenished with fresh sand, the rig was fired with natural gas as usual at a natural gas flow of 52.3 l/min (32 kW). After getting stable bed temperature raffinate was introduced into the bed at a flow rate of 2.29 l/h (3 kg/h). Experimental conditions before the raffinate introduction were noted to be BT = 800 °C and BP = 261 mmWg. Note that, Raffinate feed flow in this test is lower than that in the previous one. This is due to the fact that feed pipe of the peristaltic pump was ruptured and was replaced with a new one of smaller inside diameter and hence lower feed rate. Bed pressure

was noted to be higher (260 instead of 240 mmWg) than previous experiments with coal and raffinate, possibly due to the slight variation in the fresh sand used.

After around 10 minutes, raffinate feed was stopped due to low bed pressure. Total amount of raffinate fed into the bed during this period was 0.38 litres (0.5 kg) which translates into around 6.2% raffinate in the sand. The burner was kept running so that gas coming from the combustion chamber was still at high temperature. It was observed that BT went up slowly and BP went down to 100 mmWg. The bed and freeboard temperature and bed pressure variations during the experiment as a function of time are plotted in Figure 7.5. Magnified view of the figure showing bed behavior after raffinate introduction is shown in Figure 7.6.

Three major differences were noted between coal-raffinate co-firing and gas-raffinate co-firing.

1. With gas-raffinate bed slumped within ten minutes and with lesser amount of raffinate going into the bed as compared to coal-raffinate.
2. Bed temperature went up instead of going down as in the case of previous experiment with coal and raffinate
3. Freeboard temperature was lower than the bed temperature as opposed to coal-raffinate tests.

After 6.8 minutes of the raffinate stoppage, burner was stopped but fan was kept running. BP started going up and restored to its original value. Thus it can be concluded that agglomerates formed at higher temperature broke down to individual particles when BT dropped. With natural gas-raffinate co-firing bed slumped quickly, in lesser time and with lesser amount of raffinate feeding into the bed as compared to coal-raffinate co-firing. This is possibly due the fact that coal mineral matter, due the presence of calcium, helps preventing the agglomeration and increases operational time.

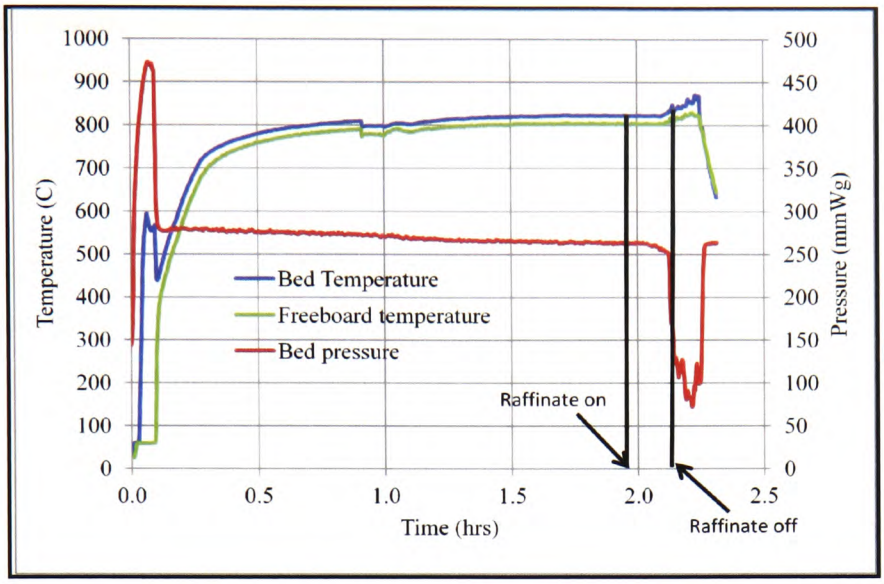


Figure 7.5: Bed behaviour during co-combustion of natural gas and raffinate

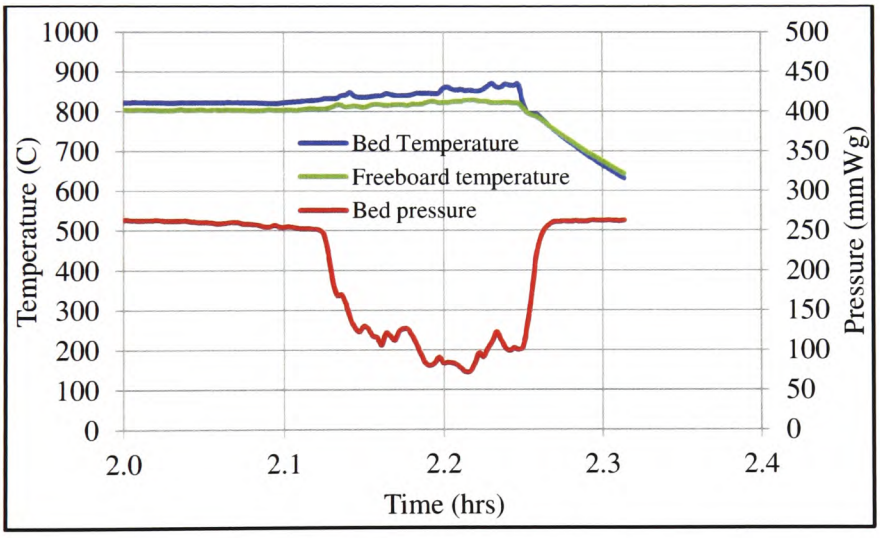


Figure 7.6: Temperature and Pressure fluctuations during Agglomeration test of Co-Combustion of Natural gas and Raffinate

During coal-raffinate firing freeboard temperature was higher than bed temperature but in the case of gas-raffinate co-firing it was vice versa. It may be possible that with coal-raffinate co-firing there might be potentially more unburned combustibles in the bed region compared to gas-raffinate co-firing and the combustion of these unburned combustibles could have

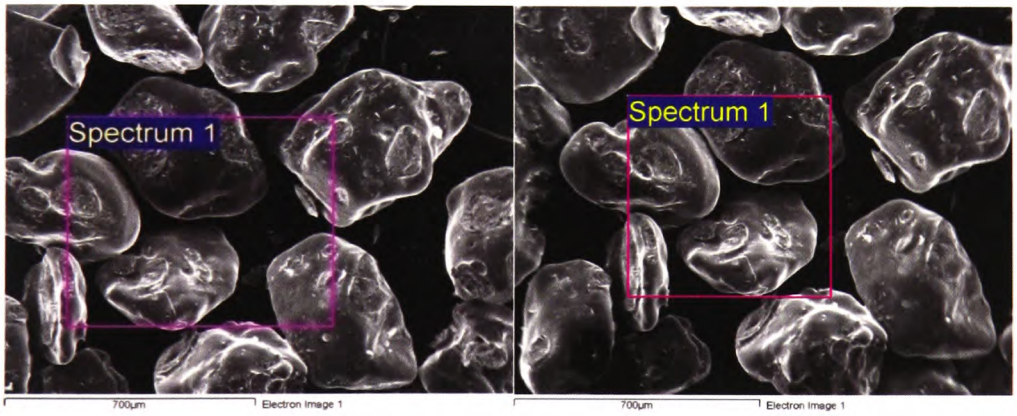
proceeded to the freeboard region. This indicates the burning of raffinate in the bed with gas firing. It picks heat from the sand to get ignited. With coal firing, as coal is already burning above the bed, it picks heat from the flame above the bed and at least part of it starts burning above the bed.

The figure shows that just before the raffinate feed was stopped both bed and freeboard temperatures started increasing and bed pressure started declining before a sudden dip which was thought to be the condition of onset of agglomeration and raffinate feed was stopped. After the raffinate feed was stopped, bed temperature kept on increasing which could be due to two reasons. Firstly, as the bed pressure was very low indicating that most of the bed was agglomerated and slumped, there was lesser sand available to be fluidised and to absorb heat from the hot flue gas coming from the bottom consequently bed temperature observed to be increased. Secondly, increase in the bed temperature may be probably due to increased combustion chamber temperature. It was observed that air flow was increased itself, possibly due to lesser resistance offered by bed as lesser sand was available to be fluidised as a result of agglomeration. As gas flow also increases with air flow proportionally due to the constant air/fuel ratio control system, a higher gas flow might have increased combustion chamber temperature. This higher combustion chamber could be responsible for higher bed temperature. It is possible that both of these factors are acting simultaneously and the increase in bed temperature is the net effect of the two.

Results of SEM analysis are given in Table 7.12 and are discussed in Section 7.11. SEM scan is shown in Figure 7.7. Flue gas analyses of the natural gas-raffinate co-combustion are given in Table 7.13. The table shows that the introduction of raffinate decreased O_2 level showing that raffinate was burning. However change in O_2 concentration was very low indicating that combustible matter in raffinate introduced was very low as compared to total fuel flow. Also emissions of CO show that raffinate results in incomplete combustion. Presence of hydrogen in the combustion products after raffinate introduction indicates the possibility of occurring water gas shift reaction.

Table 7.12: SEM results of Raffinate-Natural gas Combustion test

	Site of interest 1		Site of interest 2	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
O	51.44	65.84	50.22	64.2
F	-0.08	-0.09	-	-
Na	4.48	3.99	3.7	3.29
Mg	-	-	0.19	0.16
Al	1.23	0.94	0.85	0.64
Si	35.32	25.75	39.57	28.81
P	-	-	0.23	0.15
K	4.6	2.41	4.86	2.54
Ca	0.42	0.21	0.38	0.19
Fe	2.59	0.95	-	-



a) Site of interest 1 b) Site of interest 2

Figure 7.7: SEM scan of natural gas-raffinate test

Table 7.13: Flue gas analysis of Natural gas-Raffinate Co-Firing

	Gas only		Gas + Raffinate	
	Measured	Corrected to 6% O_2	Measured	Corrected to 6% O_2
O_2 (%)	10.6	6	10	6
CO_2 (%)	5.9	8.5	6.3	8.6
CO (ppm)	-	-	497	678
NO (ppm)	37	53	107	146
NO_2 (ppm)	-	-	7	9.5
NO_x (ppm)	37	53	114	156
SO_2 (ppm)	2	3	-	-
H_2 (ppm)	-	-	44	60

NO_x emissions after the introduction of raffinate rose considerably, unlike in the case of coal-raffinate test where they were almost same before and after raffinate introduction. This is possibly due to lower nitrogen content of natural gas which resulted in lower NO_x emissions before raffinate introduction. The NO_x emissions increased after raffinate introduction due to the fuel bound nitrogen as raffinate contains about 1.6% nitrogen in it. Presence of NO_2 is also evidenced in the flue gas after the introduction of raffinate. The balance between NO and NO_2 depends upon the nature of the nitrogen compounds present in the fuel and operating conditions. Mechanisms of NO_x formation are discussed in Chapter 6 on emissions. Increase in CO and NO_x emissions could be due to lack of temperature homogeneity caused by poor mixing and improper combustion which led to de-fluidisation. The phenomenon was also observed by Fryda *et al.* 2006.

7.10.3 Coal and Vinasse Co-Firing:

As agglomeration occurred very quickly in both the tests involved raffinate it was decided to perform agglomeration test with vinasse which has relatively lower Na and K content as compared to raffinate. The rig was fired with natural gas as usual. After achieving a bed temperature of 600 °C, coal feed was started and subsequently after few minutes the gas

burner was turned off. Finally, after the bed temperature stabilised, vinasse feed was started. The experimental conditions are given in Table 7.14.

Table 7.14: Experimental conditions for Coal-Vinasse test

Coal flow (kg/h)	2.1
Coal flow (kW)	17.5
Vinasse flow (l/h)	1.65
Vinasse flow (kg/h), Density = 1320 kg/m^3	2.2
Coal to Vinasse feed ratio (kg/h)/(kg/h)	0.95
Coal (%)	48.8
Vinasse (%)	51.2
Coal only feed time (hrs)	1.27
(Coal + Vinasse) feed time (hrs)	0.61
Total coal feed time (hrs)	1.88
Total coal feed (kg)	3.95
Total vinasse feed (kg)	1.34
Coal to vinasse mass ratio (kg/kg)*	2.95
Sand to vinasse ratio (kg/kg)*	5.6

*Based on the total fuel mass input into the bed

It was observed that vinasse behaved similar to raffinate, despite its low alkali content. Bed slumped within 37 minutes of the start of vinasse feeding. Temperature and pressure variations as a function of time are plotted in Figure 7.8. Magnified view of the figure showing bed behaviour during vinasse introduction is given in Figure 7.9. Sudden changes in bed and freeboard temperatures and bed pressure were observed as can be witnessed in Figure 7.9 and this was thought to be the onset of agglomeration process. At this stage both coal and vinasse feeds were stopped. However, there were some abnormal parameters observed.

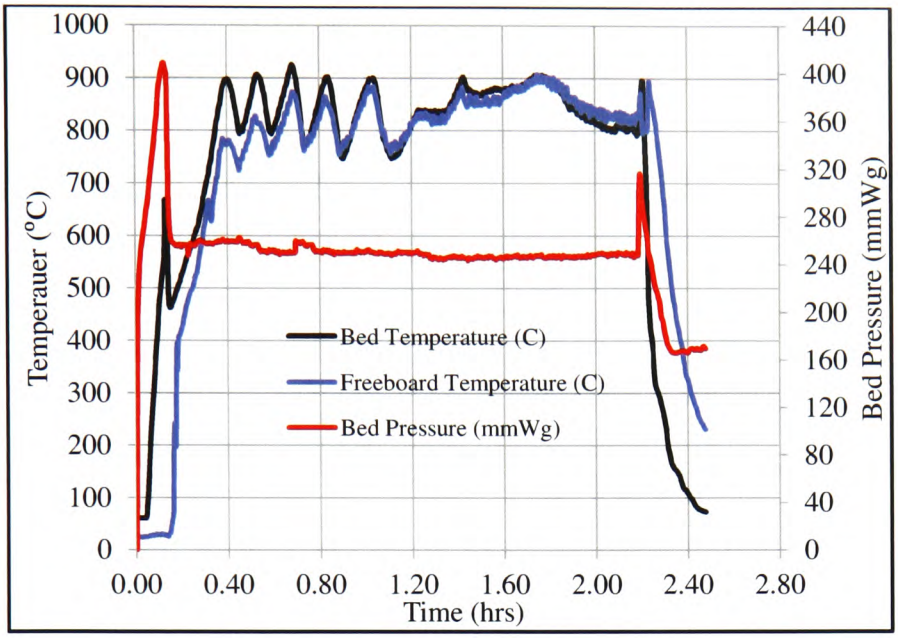


Figure 7.8: Temperature and Pressure observations during coal vinasse agglomerat test

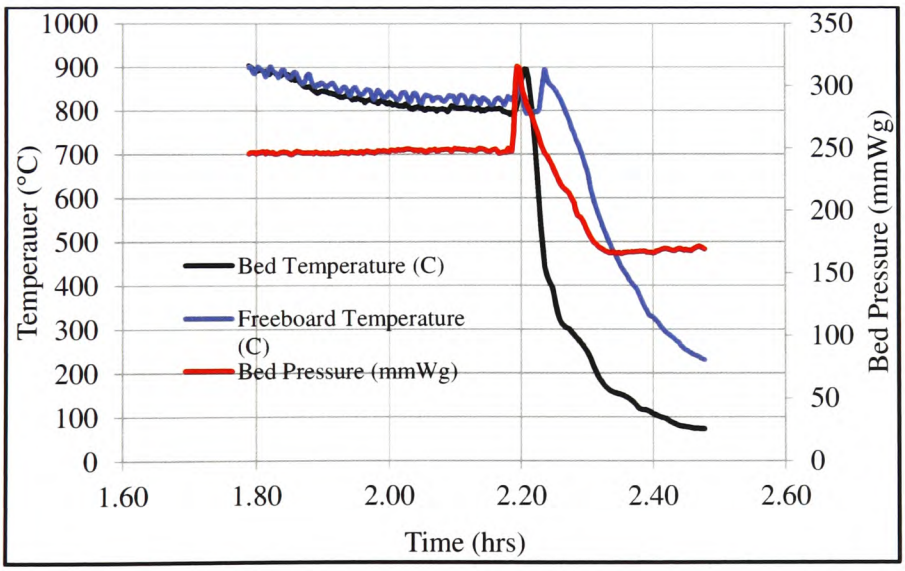


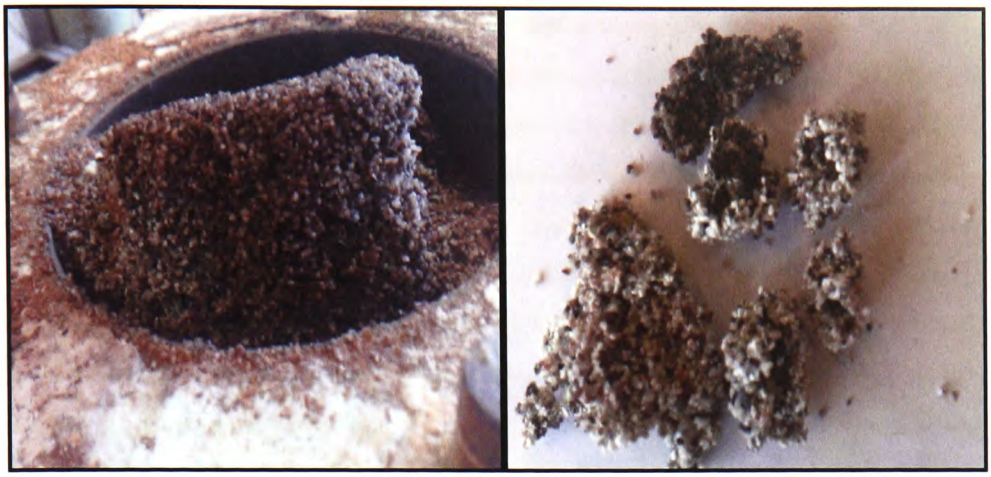
Figure 7.9: Temperature and Pressure observations during vinasse feeding

At the start of agglomeration process bed pressure went up sharply (instead of going down). However it came down after a peak.

- Bed temperature and freeboard temperature both went up at the start of agglomeration
- Soon after the onset of agglomeration freeboard temperature was considerably higher than bed temperature and was so for some time after stopping both the coal and vinasse feeds

Ash fusion temperature of vinasse is 700 °C [Cortez and Perez, 1997] but during the test the bed was slumped well above it, at around 800 °C which indicates the formation of eutectic compounds with different thermal properties during co-firing than those found in vinasse. However, the temperature measured by Cortez and Perez was not in a fluidised bed but in a refractory lined combustion chamber. Therefore, it is also possible that force of the air/gas velocity may have influenced the fusion temperature. It could also be due to higher mass of the material, sand plus ash, in the bed which resulted in its fusion and agglomeration at higher temperature.

The rig was subsequently dismantled to inspect the bed more closely and an agglomerated lump as shown in Figure 7.10a was found at the top of the bed. The lump was breakable by hand. It is interesting to note that the lump was found at the top of the bed instead of at the bottom of the bed as was found in the case of raffinate. The reason for that could be that vinasse was fed at higher level in the bed than raffinate and the lump was probably formed in the later stages of the test possibly due to lower alkali content of vinasse than raffinate. The formation of lump at the top also explains the observed increase in freeboard temperature. The lump might have contained some unburned combustibles which continued to burn which resulted in higher freeboard temperature.



(a) In-situ agglomerated material (b) Hard sintered agglomorates

Figure 7.10: Agglomerated material after Coal-Vinasse co-firing

There were found some hard sintered bed agglomerates as shown in figure 7.10b. During the tests the sampling probe of the flue gas analyser was also seen to be deposited with white material, most likely NaCl and KCl, see Figure 7.11a. There were also white deposits found on the feed pipe, see Fig 7.11b, which may be composed of alkaline compounds.

a) Deposits on feed pipe b) Deposits on gas analysis probe

Figure 7.11: Sticky deposits on the gas analysis probe and feed pipe

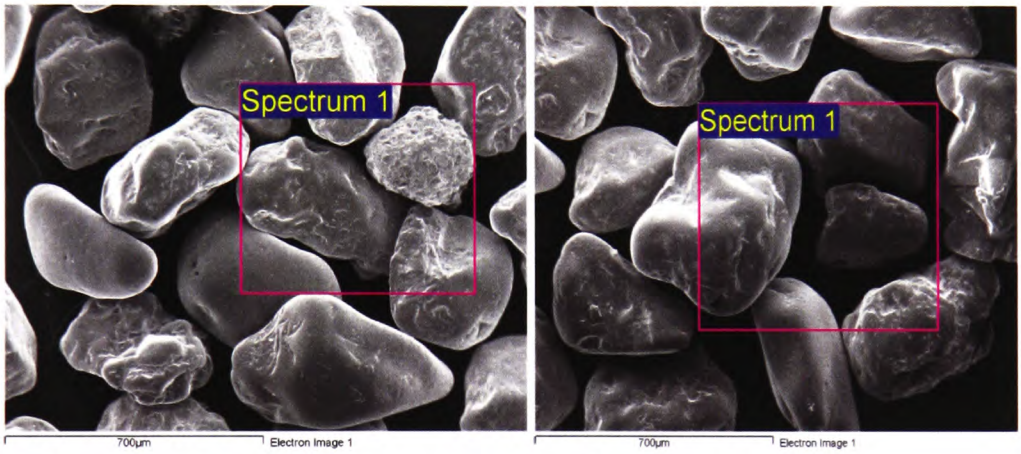
Results of SEM analysis are given in Table 7.15 and are discussed in Section 7.11. SEM scan is shown in Figure 7.12. Gas analyses of the test are given in Table 7.16. It can be seen from the table that there is an increase in SO_2 emissions when vinasse is introduced. This is because vinasse has significant amounts of sulphur in it. However the increase in SO_2 does not reflect the high amounts of 5% sulphur in vinasse. Thus it was thought that the sulphur behaved differently in the presence of water or is absorbed by water. The same phenomenon was observed during coal-PP pulp tests. The nitrogen content of vinasse was also very high, but the NO_x emissions were the same (on as measured basis) before and after the introduction of vinasse, but were found lower in the latter case when corrected to 6% O_2 basis. This could be because N in biomass behaves differently than N in coal as discussed in Chapter 6.

Table 7.15: SEM analysis of Coal-Vinasse Agglomeration test

	Site of interest 1		Site of interest 2	
Element	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
O	48.29	62.23	40.98	60.40
F	4.64	5.03	-1.76	-2.18
Na	3.46	3.1	3.37	3.46
Mg	0.3	0.26	0.4	0.39
Al	1.35	1.03	2.13	1.86
Si	28.37	20.83	23.48	19.71
P	0.26	0.18	0.23	0.17
S	2.85	1.83	3.33	2.45
K	9.84	5.19	10.22	6.16
Ca	0.63	0.32	0.82	0.48
Fe	-	-	16.8	7.09

Table 7.16: Gas analyses of the Coal-Vinasse test

Gas constituent	Coal only		Coal + Vinasse	
	As measured (12.7% O_2)	Corrected to 6% O_2	As measured (10.3% O_2)	Corrected to 6% O_2
CO_2 (%)	6.3	11.4	8.1	11.4
CO (ppm)	350	633	2234	3132
NO_x (ppm)	472	853	471	660
SO_2 (ppm)	443	801	711	997



(a) Site of interest 1 (b) Site of interest 2

Figure 7.12: SEM scan of coal-vinasse agglomeration test

7.10.4 Coal and Pressed Pulp Co-Firing:

Vinasse and raffinate agglomeration tests revealed that agglomeration occurred fairly quickly and could be problematic in fluidised beds. Consequently, it was decided to perform longer tests in which pressed pulp, having relatively lower alkali content, was co-fired with coal to assess its behaviour in the bed. The test rig was operated at a typical bed temperature of about 870°C for approximately 7 hours per day for 11 days to assess the likelihood of agglomeration over a longer term when co-firing coal and pressed sugar beet pulp. Before the

co-firing tests with coal and pulp, the rig was fired with Thoresby coal for 3 days for comparison purposes and after replacement of the bed the remainder of the tests were undertaken with a 50/50 blend of coal and pulp. Samples were removed from the bed on a daily basis for SEM analysis. Results of SEM analysis of representative samples are given in Table 7.17. There was no evidence of abnormal fluidised bed behaviour during these tests.

Moreover visual and microscopic examination exhibited no visible signs of agglomeration, see for example Figure 7.13 which presents a magnified image (SEM scan) of the sand from the bed at the end of the co-firing experiments. The visual appearance of the bed after the co-firing tests was however different from that after coal firing, see Figure 7.14 which suggests that the composition of the outer layers of the sand particles are different in the two cases.

Table 7.17: SEM results of Coal-PP Combustion test

	Coal, Sample 4 (after 3 days testing)		Coal-PP, Sample 12 (after 8 days testing)	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	29.16	38.69	52.8	57.53
O	47.12	46.94	44.35	36.28
F	2.95	2.48	1.81	1.24
Na	2.67	1.85	0.43	0.24
Mg	0.14	0.09	1.7	0.92
Al	4.16	2.45	3.9	1.89
Si	11.51	6.53	9.15	4.26
P	0.11	0.06	0.82	0.35
S	0.53	0.26	0.85	0.35
K	0.29	0.12	1.08	0.36
Ca	0.96	0.38	13.17	4.3
Ti	0.41	0.14	0.5	0.14
V	-	-	-31.14	-8

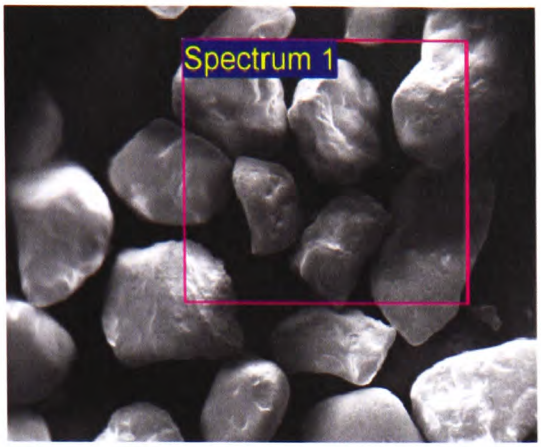


Figure 7.13: The Sand Bed after the Coal-Pressed Pulp Co-Firing Tests

a) Coal b) Coal-pressed pulp

Figure 7.14: Visual appearance of the Fluidised Bed after Extended Tests with coal and pulp

Emissions from the combustion of Thoresby coal alone and 50/50 blend of the coal and pressed pulp were compared and discussed in Chapter 6. In brief, blend of 50/50 coal and pulp gives lower NO_x and SO_2 emissions as compared to coal alone, due to lower nitrogen and sulphur content of PP.

7.11 Comparison of SEM results:

One of the mechanisms of agglomeration as described earlier is partial melting of low melting ash components to form a liquid phase of low viscosity which in turn forms necks

between the bed particles. This mechanism was thought to be dominant in the combustion of raffinate and vinasse as these materials have high alkali metal contents.

The levels of potassium with coal-PP co-firing were low but were considerably higher for co-firing test with raffinate and vinasse. However there appeared to be a gradual increase in potassium content when co-firing coal and pressed pulp. Armesto *et al.* (2002) also observed the accumulation of potassium in the bed when bed material was not changed between the runs. They observed increased amounts of potassium-calcium silicates in the bed. After 8 days (about 56 hours) of testing during current study potassium content had risen to 1.08% (which is around 4 times higher than that observed after 3 days testing with coal, see Figure 7.15. This is still a low level, when compared with that for raffinate, and as mentioned earlier there is no sign of bed clinkering. Consequently agglomeration is unlikely to be major problem when co-firing pressed pulp with coal particularly when size degradation of the sand during long term operation is taken into account. However a safe level for the potassium content cannot be predicted so that much longer timescale tests may be required for a definitive conclusion.

The levels of sodium on the outside of the ash and sand particles after co-firing were lower than those of potassium, see Figure 7.16 with no evidence of a gradual increase over the duration of the tests. Again however the sodium content after co-firing with pressed pulp is substantially below the measured value after the short duration raffinate test. The highest detected sodium levels occurred after 3 days of coal firing. However, no problems of agglomeration were experienced after these tests or after the extensive combustion tests described in Section 7.10.4 so that the presence of relatively high levels of sodium do not appear to be associated with bed clinkering. This is probably a result of the relatively high melting point of sodium silicate (1088 °C) which is significantly above the fluidised bed temperature. The relatively high level of sodium with Thoresby coal is in line with the typical value of about 4.5% in the ash of this coal. The amount of coal used in the co-firing tests was greater than in the 3 day coal alone case so that the low sodium levels with co-firing may be due to the pulp "neutralising" the deposition of sodium silicate. It is worth mentioning here that alkalis in coal and biomass behave differently during combustion.

During co-firing of coal, straw and wood chips in 20 MW multi-circulating fluidised bed with biomass content variation from 18 – 49%, Hansen *et al.* (1995) observed that output of gaseous alkali metals was not steady.

It can be observed from the Figures 7.15 and 7.16 that during coal only tests both sodium and potassium started accumulating but sodium accumulation rate is considerably higher than potassium, possibly due to higher sodium content in the coal. Comparison of the figures show that during coal-PP tests potassium content in the bed increased with time but sodium content first increased and then decreased which indicates interactive behaviour of sodium accumulation is different when PP is co-fired with coal. The figures also show that potassium and sodium content in the bed is very high after rafinate and vinasse co-firing tests. During natural gas-raffinate test relative sodium content is higher than potassium content as compared to coal-raffinate test which again indicates different behaviour of these alkalis during co-firing.

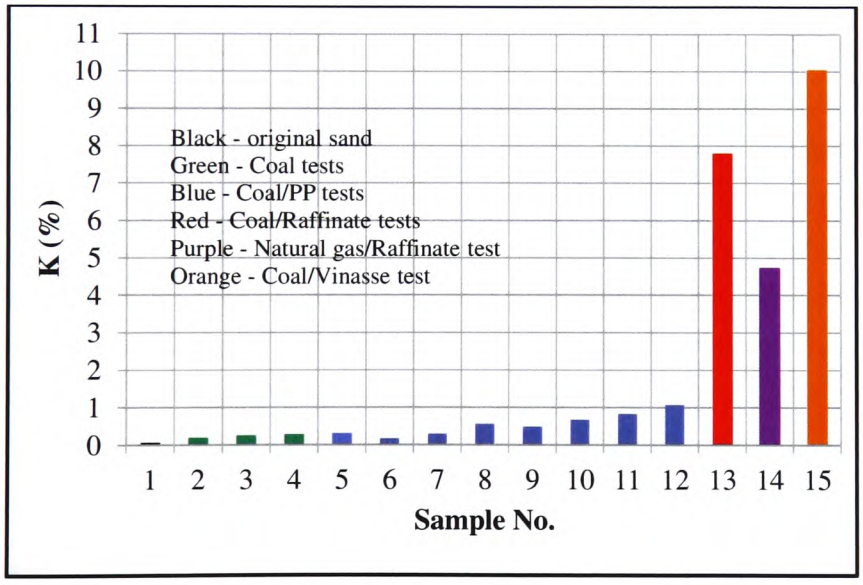


Figure 7.15: Potassium Content of the Sand Outer Layers

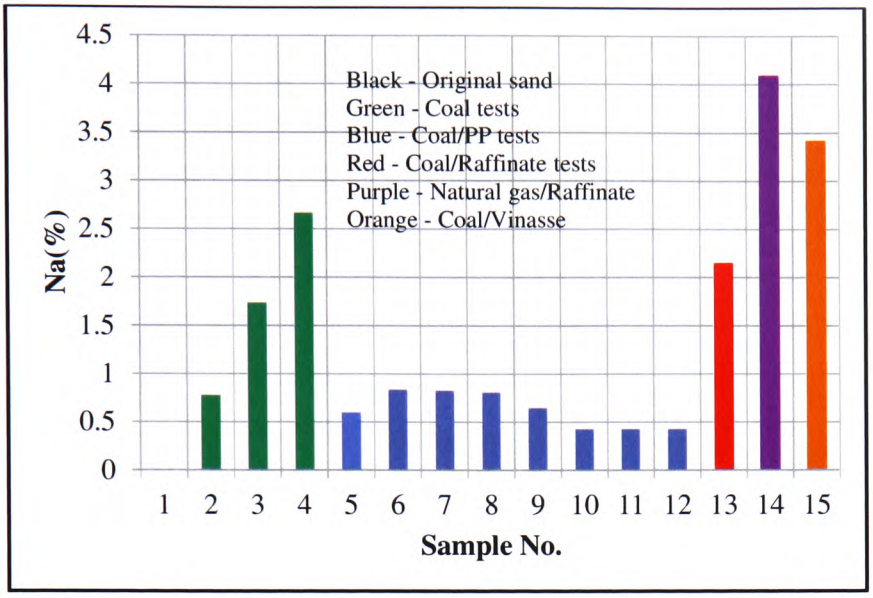


Figure 7.16: Sodium Content of the Sand Outer Layers

Potassium content in different fuels tested and their ashes is given in Table 7.18. Potassium content as percentage of ash of different fuels is shown against ash percentage of fuel in Figure 7.17. The figure is modified (y-axis extended) to include vinasse and raffinate as they were outside the scale of the original graph. The figure shows that percentage of K in ash is very high for vinasse and raffinate as compared to other biomass fuels (from literature) such as wood, paper, begasse etc. as well as pressed pulp (biomass studied during present study). The figure also shows that potassium content of pressed pulp is lower than hull, shell and pits but is higher than wood, begasse, paper etc. and is comparable with straw and grass. Thus, based on the analysis pulp has a higher propensity of agglomeration than wood and paper but is lower than hull, shell and pits. Moreover, due to their higher potassium content, agglomeration tendency of vinasse and raffinate is very much higher than some of the other biomass fuels available.

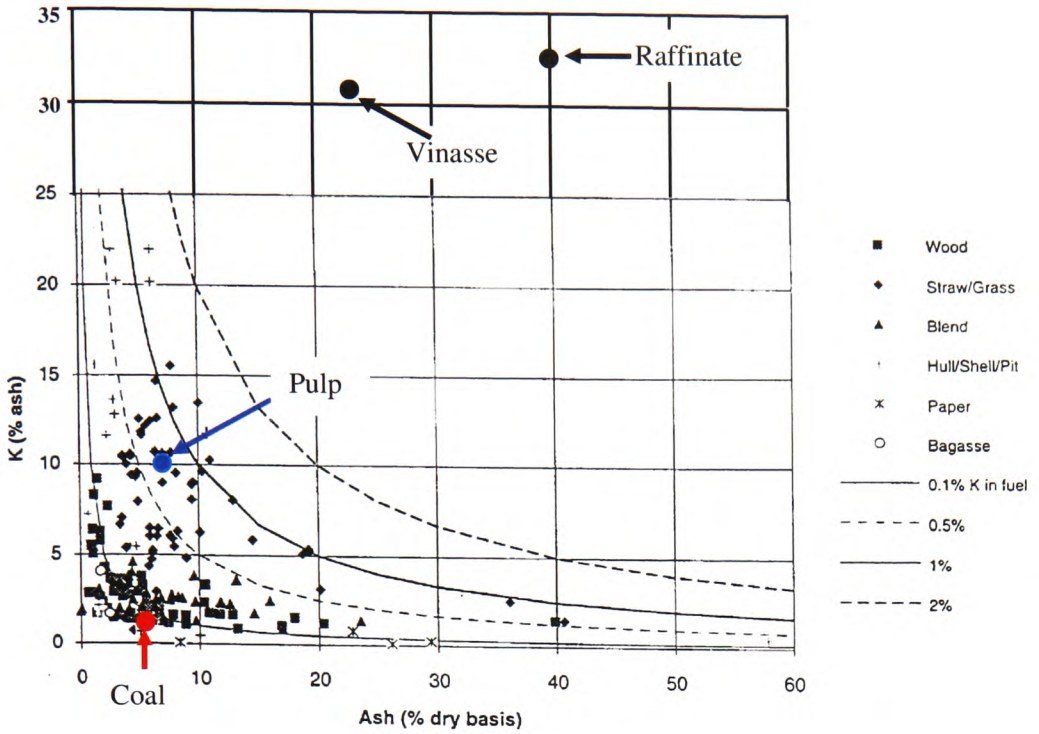


Figure 7.17: Comparison of ash potassium content in coal, pressed sugar beet pulp, vinasse and raffinate with other biomass fuels
[modified from original taken from Thomas *et al.* 1995]

Table 7.18: Potassium content of Fuels tested

Fuel	Ash (%) dry basis	K (% of Ash)	K (% of Fuel, AR)
Raffinate	40	32.5	6.5
Vinasse	23	30.4	2.94
Pulp	7	10.7	0.21
Coal	5.2	1.16	0.03

During 56 hours testing of coal-PP co-firing, almost 96 kg of PP was burned with an equivalent amount of coal in the bed. Amount of potassium introduced into the bed during this period is calculated to be 0.23 kg which equates to sand to potassium ratio of around 32.4. Results of calculations for all the experiments are given in Table 7.19. It is interesting to note that potassium introduced into the bed is the highest and sand to potassium ratio is the lowest in coal-PP test as compared to raffinate and vinasse tests. This shows that potassium

feed-rate into the bed is very important. During vinasse and raffinate tests potassium feed-rate was higher than PP test as raffinate and vinasse contain considerably higher amounts of potassium. Thus higher the amount of alkali per unit time fed into the bed higher the chances of agglomeration to occur, for explaination see column 4 of Table 7.19. It also indicates that introduction of small amount of alkali for a longer time is better than introducing larger amount in a shorter time.

Table 7.19: Potassium calculationson Fuels tested

	Fuel fed (kg)	K fed with fuel (kg)	Potassium flow (g/h)	Sand to K ratio	K in sand (kg), SEM
Coal-PP Tests (56 hours)	96 + 96	0.23	4.1	32	0.08
Coal-Raffinace Test	4.2+2.2	0.14	245.6	52	0.58
Natural gas-Raffinate Test	0.5	0.03	176.5	231	0.35
Coal-Vinasse Test	3.9+1.3	0.04	65.6	185	0.75

The table also shows, in the right column, calculated value of potassium based on SEM results, in the bed after each experiment. It can be observed that, for coal-PP test, potassium found in the bed, by SEM results, after the test is a lot lower than the potassium introduced into the bed. This could be due to evaporation of part of the potassium during the combustion process. Song, *et al.* (1999) observed that 13 – 20% potassium was evaporated with flue gas or deposited in the combustor. It can be observed that the amount of potassium accumulated in the bed, for raffinate and vinasse tests, is very much higher than the amount of potassium introduced into the bed. This shows discrepancy in the SEM results. However, it is possible that the distribution of potassium in the bed was not even. As the samples were taken from the top of the bed it is possible that this has higher potassium content as compared to the bottom. However, this theory violates the inherent nature of fluidised bed to distribute material fed into the bed equally throughout the bed. The results indicate that more research is needed to fully understand the behaviour of potassium in the fuels combusted in fluidised beds during present study.

7.12 Conclusions:

Agglomeration tests have been performed with sugar industry biomass including vinasse, raffinate and PP when co-firing with coal. The results show that raffinate and vinasse are problematic fuels and cause agglomeration fairly quickly. Calcium in coal ash extends defludidisation time which indicates that lime can be used as a bed material to increase operational times while firing these troublesome fuels. However, no signs of agglomeration were observed during prolonged tests with coal and pulp. Therefore, PP can be used as fuel in fluidised bed without the use of alkali getters as long as operational parameters are properly controlled. But, vinasse and raffinate can't be used without adapting measures such as addition of alkali getters to reduce agglomeration. It is found that accumulation of alkali as well as its feed rate to fluidised bed are two key parameters in determining agglomeration behaviour of the bed.

Chapter 8

Water Injection Tests

8.1 Introduction:

As, shown previously in Chapter 5, one of the main affects of co-firing with pressed pulp is that the moisture in the pulp cools the bed so that a specified bed temperature can be achieved with a lower air flow rate. This cooling effect would enable a higher thermal rating to be achieved on the full scale plant at Cantley since the amount of coal which can be burnt is currently restricted by limitations in the supply of fluidising gases or air. As proved in Chapter 5 that blending pressed pulp with coal is beneficial in reducing excess air required to get a stable bed temperature. However, due to potential problems with pressed pulp feeding into the bed, it may be difficult to employ this technology to enhance the capacity of the HGG. Therefore tests have been performed with simpler and consequently cheaper method of cooling the bed i.e. direct injection of water into the bed. However, Cantley personnel are concerned that this could result in excessive generation of carbon monoxide through a reverse water gas reaction as well as incomplete combustion of coal due to local cold spots. Consequently limited tests were undertaken to determine the affects of water injection into the pilot scale fluidised bed when firing Thoresby coal. In order to assess the effect of reverse water gas reaction on CO emissions, water injection tests have also been carried out with the rig being fired with natural gas. As natural gas was fired in the combustion (plenum) chamber, possibility of occurrence of incomplete combustion in this latter case is not a question.

8.2 Water injection tests:

Water injection tests have been carried out when the rig was fired with coal as well as natural gas. Water was injected into the bed through the feed tube used for vinasse and raffinate feeding as described in Chapter 3. The water was used from the mains supply and was at an average temperature of 7 °C. Compressed air was used to disperse the water over the bed evenly. Results of these tests are explained and discussed in the following sub-sections.

8.2.1 Water injection with Coal Firing:

The first set of tests involved injection of high water flow-rate of 11 l/hr into the bed which was stable initially at a temperature of 900°C. Under these conditions the bed temperature gradually decreased until the water injection was turned off, see Figure 8.1, and at this point the bed temperature started to increase again. It is clear that CO emissions are high (≥500 ppm) only at bed temperatures below about 750°C. This temperature is well below that associated with the water gas reaction which suggests that high CO levels are caused by incomplete combustion. It is also much lower than the operating temperatures at Cantley so that it appears that the generation of high levels of carbon monoxide and hydrogen are unlikely on the full scale plant. This is confirmed in Figure 8.2, which presents data for both CO and hydrogen levels in the freeboard gases during the same test. Again significant levels of hydrogen are only present at low bed temperatures and this is likely to be due to incomplete combustion of the volatiles under these conditions. It is also possible that injected water may have produced CO and H_2 by the following reaction [Suyitno, *et al.* 2011] with char.

$$C + H_2O \rightarrow CO + H_2 \Delta H_{298}K = 131.4 \text{ kJ/mol} \quad (8.1)$$

Finally, Figure 8.3 presents a comparison between the CO concentrations when water was injected (i.e. bed temperature decreasing) and the period of the test when the water injection was turned off (i.e. bed temperature increasing). Relatively higher amount of CO during water injection (BT going down) also suggest the occurrence of above reaction.

Further tests were carried out under steady state conditions in which the coal, water and air flows were varied. Again there is little evidence that the water gas reaction results in higher CO or hydrogen emissions even at the higher temperatures where the effect would be most significant.

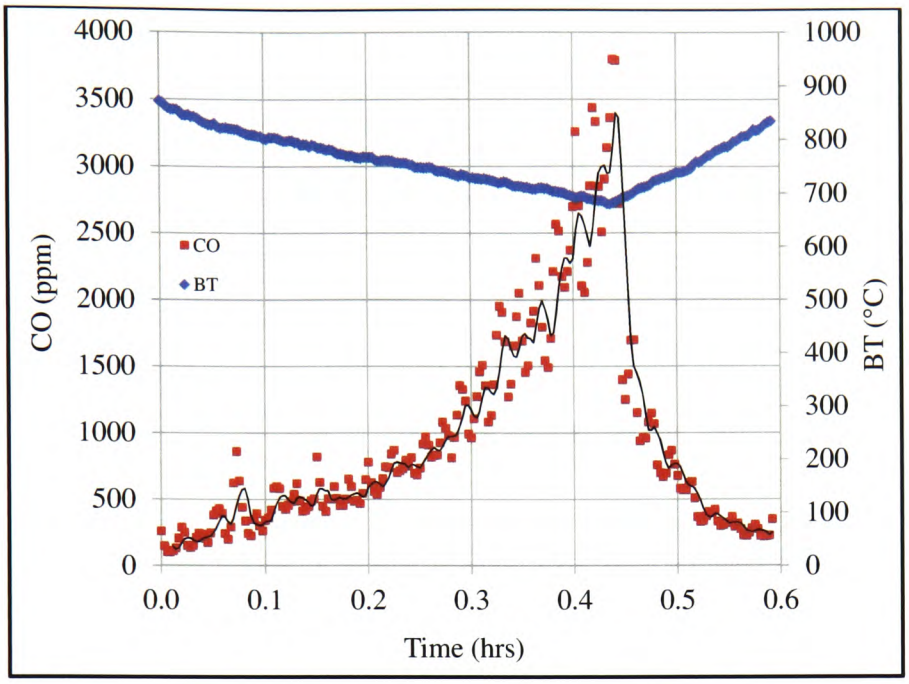


Figure 8.1: Variation of BT and CO emissions during water injection test with Coal

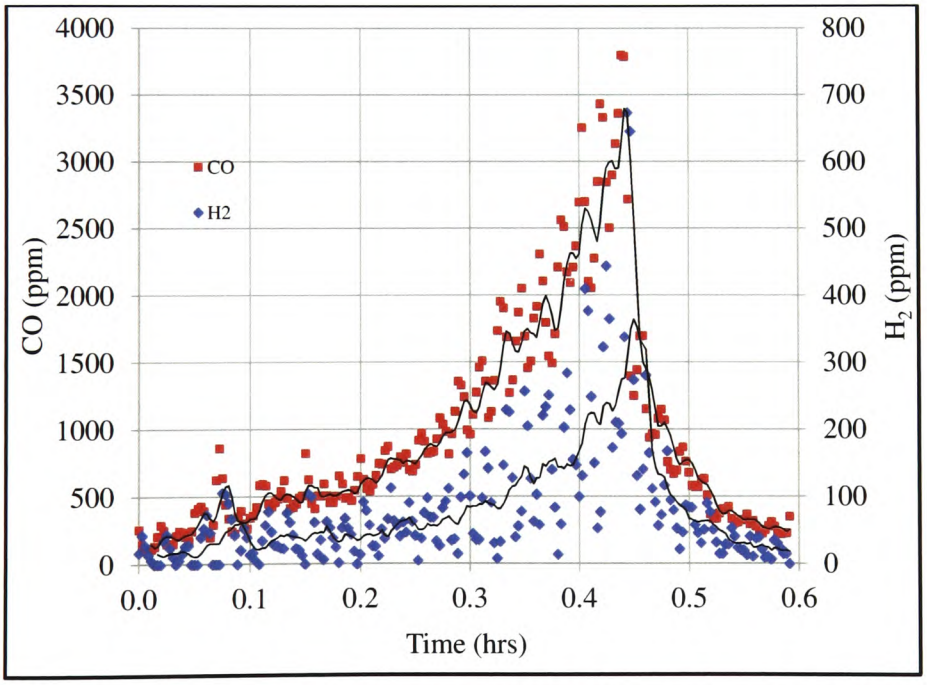


Figure 8.2: CO and Hydrogen Concentrations in the Freeboard during water injection test with Coal

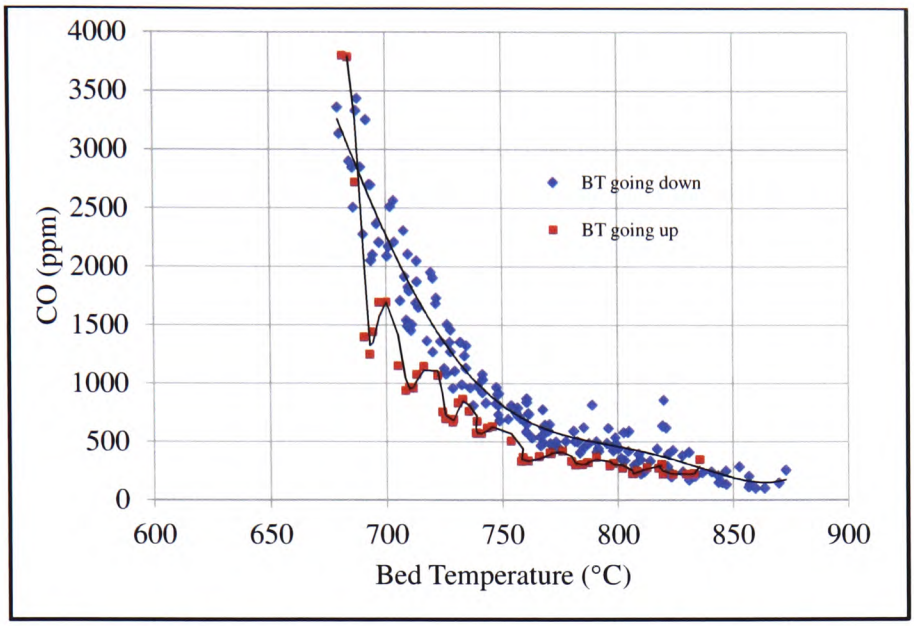


Figure 8.3: CO Emissions before and after water injection with Coal

In order to find out the effect of water flow rate on bed temperature as a function of coal input, the rig was fired at two different coal inputs, 11 and 17.2 kW, with and without water injection. The bed temperature in both the tests without water injection was stabilised at 880°C. The results are given in Table 8.1, which shows operational parameters as well as exhaust gas emissions corrected to 6% O_2. The gas measurements are taken as dry gas. The table shows comparison of the two tests with and without water injection at same air flow of 40m^3/h for coal inputs of 17.2 kW (coloured red for clarity). The results show that CO and H_2 concentration in the flue gas increased by 176 ppm and 14.4 ppm respectively, after water injection possibly due to incomplete combustion. This argument is also justified by increase in O_2 concentration in the flue gas although this only increases by 0.1%. Emissions of NO_x remained the same before and after water injection which again justified the arguments mentioned in Chapter 6 that the NO_x emissions were not affected by moisture in fuel.

Table 8.1: Results of Coal Combustion tests with and without water injection

Air Flow m^3/h	Bed Temp °C	Water Flow l/h	Mass Ratio of Water Flow to Coal Flow	O_2 %	CO ppm @ 6% O_2	H_2 ppm @ 6% O_2	NO_xppm @ 6% O_2
Coal Flow = 1.36 kg/h (11 kW)							
32.5	880	no	0	16	1695		820
32.5	Not stabilised	4.5	3.3	17.3	6523		657
Coal Flow = 2.13 kg/h (17.2 kW)							
40	880	No	0	11.8	498	24.6	754
40	802	3.4	1.60	11.9	674	39.0	754
32.5	870	4.5	2.07	13.8	4104	-	824

The table also shows data for the same water flow and bed temperature when the bed was fired at different thermal inputs. The data shows that at lower coal input of 11 kW and higher water flow rate of 4.5 l/h (water to coal mass ratio = 3.3), bed temperature did not stabilise. Calculations show that more than 5kW energy is required to evaporate this amount of water at the bed temperature, which leaves less than 6 kW to maintain the temperature of the bed which is not sufficient. However, at higher coal input of 17.2 kW and lower water flow of 3.4l/h (water to coal mass ratio = 1.6), bed temperature stabilised with a drop in temperature of just under 80 °C. In this latter case only 4 kW is required to evaporate the injected water which leaves more than 13kW to maintain the bed temperature. Thus, at higher water to coal mass ratios it is difficult or even impossible to maintain bed temperature due to higher amount of energy being used to evaporate water. The data also shows that at higher water to coal mass ratio of 3.3, CO emissions (6523 ppm) are very much higher relative to those (674ppm) at lower water to coal mass ratio of 1.6. However, as can be observed form the data the CO emissions are higher in the case of 11 kW input than that in the case of 17.2 kW, even without water injection. It may be due to due to excessive carryover of coal dust by higher air velocity. It could also be due to reduction in the effective mixing of air and volatile and diffusion of air into the coal. Slight increase in hydrogen level after water injection in the

case of 17.2 kW may also be due to incomplete combustion (gasification) or water gas reaction. Thus, it can be concluded from above discussion that higher CO emissions may be due to incomplete combustion as a result of combined effect of higher excess air as well as water injection.

Drop in bed temperature due to water injection can be compensated by reducing air flow. In order to investigate this, another test was carried out with the same coal input (17.2 kW) at different air flows (40 and 32.5 m^3/h), and with 4.5 l/h water inflow and without water injection. The data is shown in lower part of Table 8.1. It can be observed from the data that there is very little difference in bed temperatures in both cases due the fact that drop in bed temperature due to water injection is partially compensated by reduced air flow. Almost same bed temperature is achieved with 7.5 m^3/h drop in air flow with 4.5 litre water inflow. Thus, keeping air flow constant more coal can be fed into the bed to get the same bed temperature if water in injected. This excess air can be used to burn around 5 kW equivalent of more coal and thus result in increase in thermal capacity by around 30%. However, in the case of water injection emissions of CO are around 10 times higher than those without water injection. This makes necessary to use secondary air to burn the unburned fuel in the freeboard. Cantley's hot gas generator (HGG) has got this capability.

A range of tests have also been carried out in order to further investigate the effects of reduction in the combustion air supply, at constant rate of water injection, at two different coal inputs. The results are shown in Table 8.2. The data shows that at same coal and water inflows, bed temperature increases with decrease in air flow.

At two different coal inputs, 17.2 and 14 kW, and same water inflow (3.4 l/h), with water to coal ratios of 1.6 and 1.97, almost same bed temperature was achieved at 37 and 34 m^3/h air flows respectively. Thus, the higher the water to coal ratio, the lower the air flow required to get the same bed temperature. Putting into perspective, this shows that by introducing 3.4 l/h of water into the bed, an equivalent of 3.2kW more coal can be fed into the bed to get the same bed temperature. This equates to an increase in throughput of around 23%. However, emissions of CO are little bit higher at reduced air flow. The data, in Table 8.2, also shows that the same bed temperature of 820 °C can be achieved at even higher coal input of 22.7 kW with water inflow of 8 l/h but at slightly higher air flow of 44 m^3/h. But in this latter case

CO emissions are 4 – 6 times higher than the previous cases. This could be due to higher water inflow. As it is mentioned earlier, water injection may have resulted in poor mixing of air with fuel and thus resulted in higher CO emissions. It is also possible that higher CO emissions are due to higher coal input. At increased coal input, volatiles are released in larger amount and may have left the bed unburned. This latter argument is also justified by the lower O_2 level in the flue gas in the latter case (8.6%) as compared to 10.3% and 11.2% in the previous two cases. Around 12 – 15 times increase in H_2 in the latter case as compared to the previous two cases also represents incomplete combustion as well as the possibility of the water gas reaction occuring.

Table 8.2: Results of water injection tests with Coal at different air flows

Air Flow m^3/h	Bed Temp °C	Water Flow l/h	Mass Ratio of Water Flow to Coal Flow	O_2 %	CO ppm @ 6% O_2	H_2 ppm @ 6% O_2	NO_xppm @ 6% O_2
Coal Flow = 2.13 kg/h (17.2 kW)							
40	802	3.4	1.60	11.9	674	39.0	754
37	820	3.4	1.60	11.2	683	38.1	719
34	910	3.4	1.60	9.5	584	54.3	710
Coal Flow = 1.73kg/h (14.0 kW)							
37.5	770	3.4	1.97	12.3	703	32.1	837
34	830	3.4	1.97	10.3	860	30.0	664
30	890	3.4	1.97	9.4	532	32.4	679
Coal Flow = 2.80 kg/h (22.7 kW)							
44	820	8.0	2.86	8.6	3695	458	428
48.5	740	8.0	2.86	10.7	2877	241	439

The results of coal experiments with and without water injection are compared in Figure 8.4. The figure shows bed temperature as a function of O_2 in flue gas at a fixed power input, with and without water injection. The data for coal firing without water injection shown in the plot is at two different inputs, 16.3 and 18.2 kW, as coal data without water injection at 17.2 kW

is not available. It is assumed here that the data for 17.2 kW input without water injection falls in the same range as 16.3 and 18.2 kW. Comparison of the data shows that in order to get a bed temperature of 850 °C, O_2 in the flue gas needs to be around 12.4%, but with 3.4 l/h water injection the temperature can be achieved at around 10.7% O_2 in the flue gas. This shows that with water injection, less amount of air is required to maintain the bed temperature at a certain level as compared to that what is required without water injection. Similar observations can be made from Figure 8.5 which plots bed temperature as a function of O_2 in the flue gas at around 14 kW input from coal, with and without water injection. Again it can be observed that to achieve a bed temperature of 850 °C at 14 kW, O_2 in the flue gas needs to be 12.2% in the case of no water inflow but drops down to 10.2% with 3.4 l/h water inflow. Although the data is shown as percentage of O_2 in the flue gas, it translates into lower overall air flow requirement with water injection as compared to that without water injection.

Thus, to get a fixed bed temperature for a fixed air flow rate, more coal can be fed into the bed if water is injected. Therefore, it can be concluded that cooling effect of injected water may be able to make it possible to achieve enhancedthroughput of 40 MW, HGG of British Sugar's Cantley factory. As it is mentioned in the beginning of this chapter that the main aim of this work was to assess the possibility of occurrence of water gas shift reaction, no effort has been made to find out upper and lower limits of water flow rate into the bed.

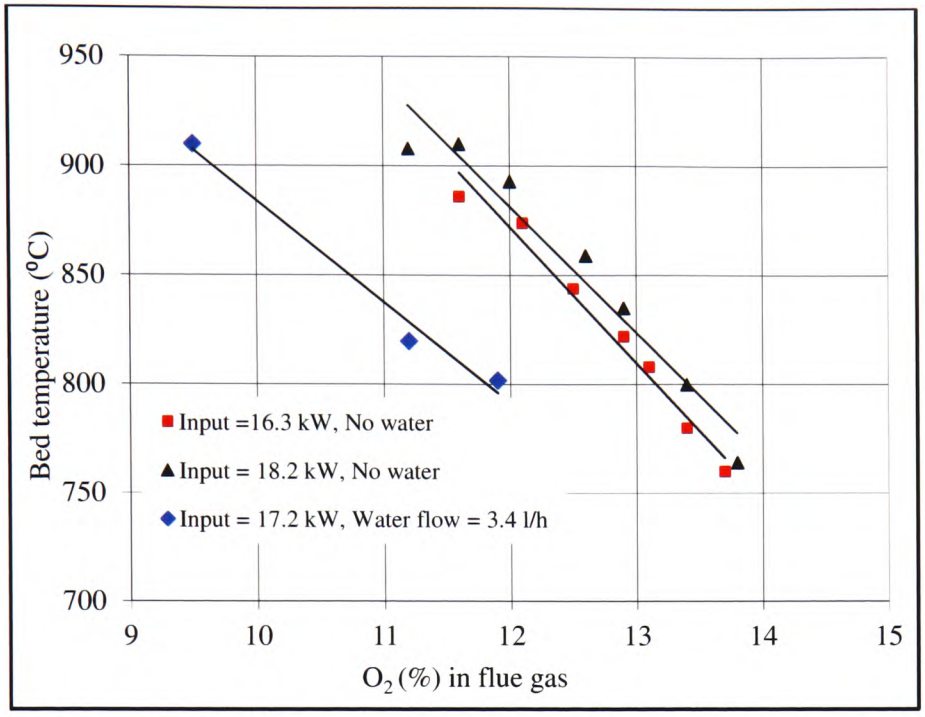


Figure 8.4: Comparison of Air requirement with and without waterinjection at 17.2kW

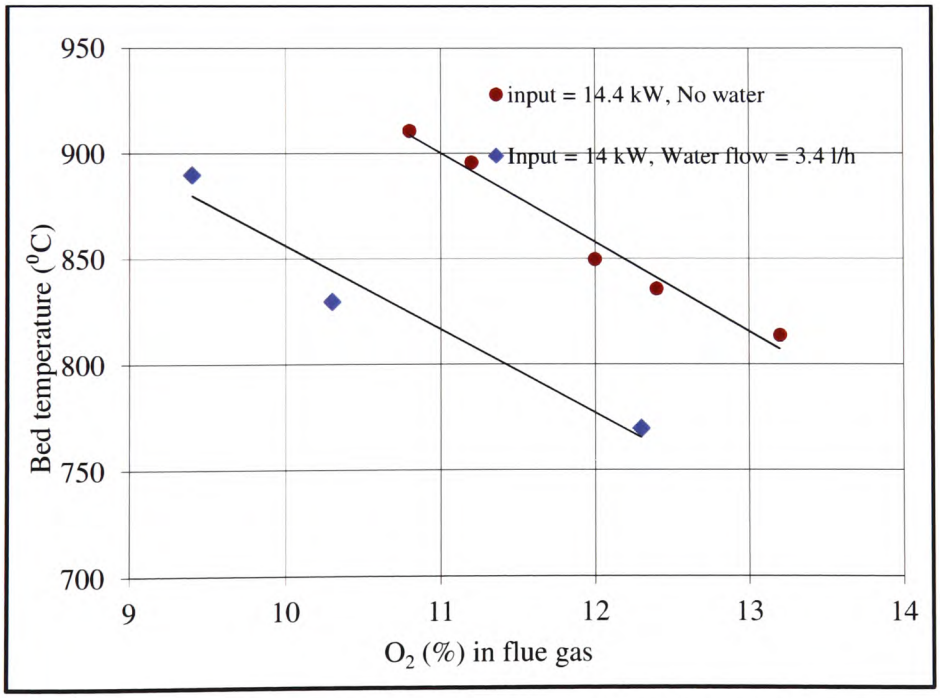


Figure 8.5: Comparison of Air requirement with and without waterinjection at 14kW

8.2.2 Water injection with Natural Gas Firing:

As discussed above, during coal firing CO emissions tend to increase when water is injected into the bed. This may be due to incomplete combustion due to local cold spots in the bed or due to production of CO by reverse water gas reaction or combination of both. In order to check the effect of water gas reaction on CO emissions, a few tests have been performed with water injection while the rig was fired with natural gas. The flow of natural gas was maintained at 66 l/min (36.3 kW) with 9.7% O_2 in the flue gas for easy comparison. Water was introduced at a rate of 9.6 l/h at BT of 840 °C. Within 18 minutes of water introduction BT went down to 667 °C, a drop of 173 °C.

Table 8.3 shows emissions from the test before and after water introduction, as measured and corrected to 3% O_2. The table shows that emissions of CO decreased slightly while those of H_2 increased slightly, indicating the possibility of occurring water gas shift reaction which can covert CO to CO_2 by the following reaction. However, figures don't show any change in CO_2 missions. This may be due to scale of measurement as CO is measured in ppm while CO_2 is in percentage. Moreover, change in CO emissions after water injection is insignificant to have any impact on CO_2 emissions.

$$H_2O + CO \rightarrow CO_2 + H_2 \Delta H^{\circ}_{298} = -41.1\ kJ/mol \quad (8.2)$$

Table 8.3: Emissions from Natural gas with water injection test at 9.6 l/h water flow

	Before water introduction		After water introduction	
	Measured	Corrected to 3% O_2	Measured	Corrected to 3% O_2
O_2 (%)	9.7	-	9.7	-
CO_2 (%)	6.4	-	6.4	-
CO (ppm)	1.2	1.9	1	1.6
NO_x (ppm)	35.1	55.9	35.7	56.9
SO_2 (ppm)	0	0	0	0
H_2 (ppm)	1.1	1.8	2.5	4.0

Another test was performed with water flow reduced to 5.3 l/h with all the other conditions being same as in the previous test. Bed Temperature went down to 772 °C within 9.5 minutes and stabilised. Time taken to reach stable temperature of 772 °C in this case is lower than that at 9.6 l/h (18 minutes) but the bed temperature in that case stabilised at 667 °C. Bed Temperature difference before and after water feeding is also lower than that in the previous case, 68 °C as compared to 173 °C, possibly due to lower water flow rate in this latter case.

Table 8.4: Emissions from Natural gas with water injection test at 5.3 l/h water flow

	Before water introduction		After water introduction	
	Measured	Corrected to 3% O_2	Measured	Corrected to 3% O_2
O_2 (%)	9.7	-	9.7	-
CO_2 (%)	6.4	-	6.4	-
CO (ppm)	1.2	1.9	0	0
NO_x (ppm)	35.1	55.9	36.2	57.7
SO_2 (ppm)	0	0	0	0
H_2 (ppm)	1.1	1.8	4.1	6.5

Emissions data from the test is given in Table 8.4. Surprisingly there is no CO but H_2 is little bit higher than that observed during previous test at higher water flow rate of 9.6 l/h. This indicates that water gas shift reaction in this case is stronger than that in the previous case and all the CO is converted to CO_2. Again no change in CO_2 is observed due to the same reason explained above. Again, change in CO emissions is insignificant to be considered important.

Third test was performed with water flow rate reduced even further to 3.6 l/h. Bed temperature in this case stabilised at 778 °C (drop of 62 °C) within 15 minutes. Drop in temperature is higher than expected as compared to the previous two tests. Expecting a linear relationship between water flow and bed temperature drop, at 3.6 l/h water flow drop in BT should have been around 25 – 30 °C. The higher than expected drop in BT can be explained on the basis of drop in BP. It was observed that BP dropped down to 225 mmWg. The drop in BP corresponds to lack of fluidised bed material thus smaller amount of bed material (around

90% of total) was available to receive water which may have resulted in higher BT drop. Unfortunately, emissions data for this test could not be recorded due to instrument fault.

The argument was also justified by the observed increase in air flow (from 80 to 83 m^3/h) which may have resulted in lower bed temperature than expected. Air flow could have been increased due to lesser resistance offered by reduced amount of bed material. This higher air flow resulted in higher mass of flue gas carrying more energy and thus leaving less energy available to raise the bed temperature.

Table 8.5: Operational data of Natural gas with water injection test

Water flow (l/h)	Initial BT (°C)	Final BT (°C)	Change in BT (°C)	Evaporation energy (kW)
9.6	840	667	173	10.3
5.3	840	772	68	6
3.6	840	778	62	4.1

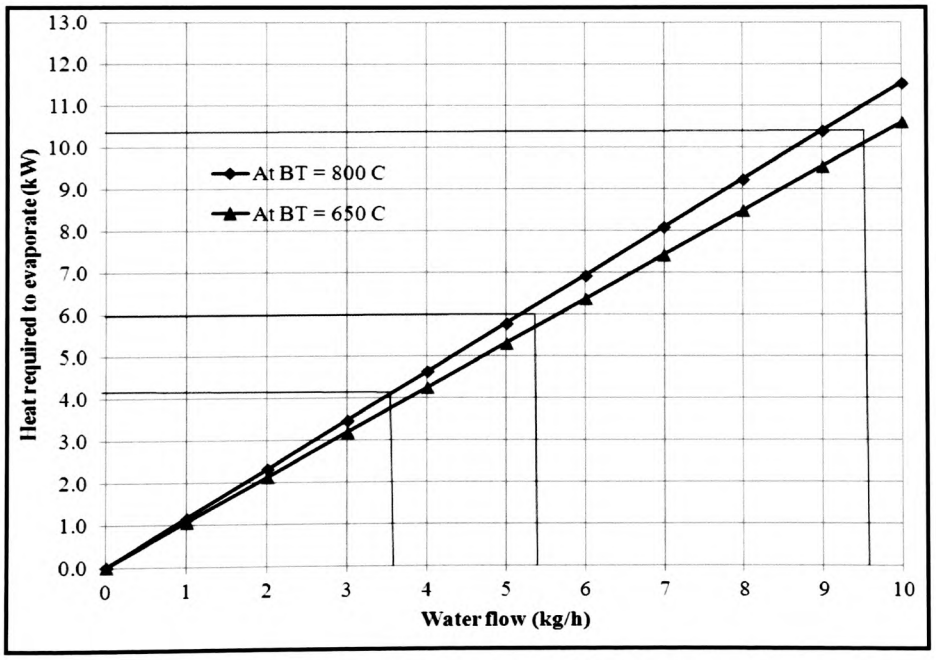


Figure 8.6: Natural gas-water test results

Operational data of the tests is given in Table 8.5. The table shows that the higher the water flow rate, the higher the drop in bed temperature due to higher amounts of energy required to evaporate the injected water. The table also shows the calculated amount of energy required to evaporate water and raise its temperature to the bed temperature. Calculated energy requirements for water to convert to steam and to raise the steam temperature to a certain temperature are plotted in Figure 8.6. The plot shows heat required to raise temperature of injected water to the temperature of the bed, as a function of water flow into the bed, at two different temperatures, 800 °C and 650 °C assuming that the steam produced by the evaporation of injected water leaves the bed at the temperature of the bed. It is clear from the figure that higher the amount of water injected into the bed, higher the amount of energy required to evaporate it. The energy requirement also increases with increase in bed temperature. At lower water flow rates difference between energy requirements at different bed temperatures is lower, and increases as the water flow is increased e.g. at a water flow rate of 10 l/h, energy requirement increases from 10.6 kJ at 650 °C to 11.6 kJ at 800 °C, an increase of around 8.6%. Energy requirement for the water flow rate used in the above tests, see Table 8.5, is also elaborated on the Figure.

Vertical lines in the figure show water flow rate used during the tests and horizontal lines show the calculated amount of energy required to evaporate that water and raise its temperature to the bed temperature. It is clear from the figure that for the tests with 3.6 l/h water flow, energy requirement is little bit outside the range of the plot i.e. the stable bed temperature should have been around 810 – 815 °C, rather than the measured value of 778 °C. Thus, in this particular case, drop in temperature of the bed is higher than it should have been, which as mentioned above could be due to smaller amount of fluidised bed material to accept relatively higher amount of water and due to increase in air flow as a result of lesser resistance offerend by reduced amount of fluidisable bed material.

Comparison of these results with gas firing tests discussed in Chapter 4 shows that at 9.7% O_2 in flue gas, bed temperatures of 772 °C and 778 °C can be achieved at 20.5 kW and 22 kW, respectively. This indicates that around 15.5 kW and 14 kW has been used by water at 9.6 and 5.3 l/h water flow rates which is higher than calculated values of 10.3 and 6 kW, respectively. The difference is higher at lower water flow rate. The difference in calculated

and actual energy required to evaporate water may be due to the effect of water injection. Bed temperature drops as a result of water injection and to get the same bed temperature at the same excess air more energy input is required. The higher amount of energy loss may also be, partly, due to increased mass flow of flue gas as a result of steam which may have resulted in higher amount of heat loss through the walls of the containment tube to the surroundings.

8.3 Conclusions:

The results of water injection tests show that a stable bed temperature was achieved at water to coal mass flow ratios as high as 2.86. However, the combustion process was not sustainable at water to coal ratio of 3.3. Therefore, there is a limit on the quantity of water which can be injected into the fluidised bed. It should also be noted that during coal-PP co-firing combustion was not sustained when 60% PP was blended with coal. For this blend water (moisture in PP) to coal ratio is calculated to be around one. Therefore, it can be concluded that it is not the amount of moisture in the pulp but the presence of pressed pulp around coal particles hinders the access of oxygen to it and thus stops combustion. Moreover, as combustion process with water injection is stable at higher water to coal ratios, it can be concluded that water injection may be more effective in increasing the capacity of the HGG.

However, the results show that water injection reduces the air requirement for achieving a fixed bed temperature i.e. for water to coal ratio of around 2, air requirement to get the same bed temperature of about 880 °C is reduced by 7.5 m^3/h (18.7%). When firing 50/50 coal-PP blend, water to coal ratio of 0.7, data analysis have shown that the same bed temperature can be achieved with about 20% less air as compared to coal firing alone. Thus, water to coal ratio is not a very good way to compare performance of fluidised bed in these two cases and one method cannot be preferred over the other without full scale trials.

Emissions of CO increase when water is injected into the fluidised bed fired with Thoresby coal. However, the split between the CO originating from incomplete combustion and that resulting from reverse water gas reaction is not quantifiable. However, water injection tests with natural gas have shown that CO produced by water gas shift reaction is insignificant. Air requirement for maintaining a fixed bed temperature decreases when water is introduced into the bed fired at fixed power input. Thus, in order to maintain a fixed bed temperature at a

fixed air flow rate, more coal can be introduced into the bed when the bed is cooled by water injection. An increase of up to 30% in throughput is observed. However, relationship between increased amounts of coal input at a certain amount of water injection is not established. The water injection flow should be controlled to replace overly excess air to maintain a stable bed temperature and the air flow needs to be sufficient to ensure complete combustion of fuel and should not be compromised. However, there is a limit of how much water can be injected, assuming that it is uniformly dispersed onto the bed. Firstly, it is dictated by the limit of optimal bed temperature achievable to sustain stable combustion (combination of effective radiation, convection and conduction heat transfer). Secondly, while the overly excess air is being gradually displaced the overall air-fuel ratio reduces and this should not be in any case reduced to less than the optimal value required for complete combustion. This optimal air/fuel ratio is likely to be higher with water injection due to the possible reasons of poorer mixing of air and volatiles and reduced diffusion of air into coal.

Chapter 9

Conclusions and Future Recommendations

9.1 Introduction:

This thesis was carried out with a view to assess the feasibility of co-firing biomass i.e by-products of sugar production process, with Thoresby coal in a fluidised bed. The study was aimed at increasing the capacity of an underperforming fluidised bed hot gas generator at the British Sugar Cantley site. Efficiency of the process and its environmental performance are evaluated by calculations based on the data gathered during the tests. Moreover, the potential problem of agglomeration when firing high alkali biomass in fluidised beds was also investigated. Finally, a relatively cheaper option i.e. injection of water into fluidised bed is studied as a potential mean to enhance the performance of the fluidised bed hot gas generator. The main conclusions arisen from this PhD study and recommendations for future work are given in the following paragraphs.

9.2 Conclusions:

Conclusions have been drawn on the basis of data analysis, calculations and observations made during the tests. The conclusions are divided into different sub-sections depending upon their relevance.

9.2.1 Feeding problems:

Feeding problems were observed with pressed sugar beet pulp. The pulp was unable to flow consistently through the screw feeder due to its very high moisture content and sticky nature. However, when it was mixed with coal the blend was able to flow through the screw feeder more smoothly and no feeding problems were observed. However, it is observed that the blend tends to bridge in the feed hopper and needed poking from time to time.

9.2.2 Temperature profiles:

During co-firing, temperature profiles in the fluidised bed i.e. bed and freeboard temperatures are dependent on the mass fraction of different fuels in the blend. Biomass fuels have lower energy density as compared to coal and thus lower stoichiometric air requirement. Therefore, variation in the proportion of biomass in coal-biomass blend varies temperature profiles. For example, during the tests the freeboard temperature was found to be lower than bed temperature due to heat losses through the walls of the containment tube. Difference between the bed and the freeboard temperature is the highest in the case of coal only firing followed by co-combustion and biomass due to increased volatile burning in the freeboard region in the case of increased biomass input as biomass contains almost twice the amount of volatiles than that of coal and lower fixed carbon. Blends of biomass and coal behave between the two extremes. Moreover, for the same power input, freeboard temperature is higher while bed temperature is lower, in the case of biomass only firing than co-firing due to over bed burning of volatiles. The difference in bed and freeboard temperatures is higher in the case of co-firing than in the case of biomass only firing due to increased amount of volatiles burning in the freeboard in the latter case.

Both bed and freeboard temperatures decrease with increases in excess air. Moreover, the gap between bed and freeboard temperatures decreases with increase in excess air and at a certain excess air level both temperatures profiles cross each other. The point of intersection of the temperature profiles varies from fuel to fuel. During coal combustion the bed and freeboard temperature profiles cross each other at lower temperature and higher excess air levels as compared to biomass and blends. Increase in the amount of excess air results in increase overbed burning. For example, in the case of co-combustion of 50/50 coal and pressed pulp blend, at 10% O_2 in the flue gas bed temperature is higher than freeboard temperature while at 11% O_2 freeboard temperature is higher than bed temperature, which demonstrates the increased amount of volatiles burning in the freeboard at higher excess air levels.

During coal and pressed pulp co-firing, freeboard temperature (relative to the bed temperature) is higher at higher excess air levels and suggests that considerable overbed burning may occur as a result of the high levels of volatiles in the pulp and or fines which could have been carried over by higher velocities at higher excess air levels. Nevertheless,

because of scatter in the data from blend to blend, uncertainties in the calorific value of the pulp, and the relatively low proportion of the thermal input contributed by this material, it is difficult to estimate the proportion of the pulp which burns above the bed. However analysis of the results for the three blends which were tested suggests that at least 50% of the pulp burns above the bed and that this would be a reasonable value to use when considering the behaviour of pressed pulp combustion in the fluidised bed of the full scale plant.

Fuel moisture has a considerable effect on the temperature profile in the fluidised bed. The highest proportion of secondary fuel which can be successfully burned depends upon the characteristics of the secondary fuel particularly moisture content. During this study it was observed that it was not possible to burn coal-PP blend containing more than 50% PP due to very high moisture content of PP. The increase in moisture content reduces the calorific value of the fuel so that the energy released by combustion is not enough to sustain the combustion process and the bed temperature drops to very low levels and combustion becomes unsustainable. For example, bed and freeboard temperatures of wood chips and coal blend with overall moisture content of 30% were found to be on average 50 °C lower than those with the blend having 10% overall moisture.

9.2.3 Fluidised Bed Efficiency:

Fluidised bed efficiency based on freeboard temperature is found to be higher than that based on bed temperature due to overbed combustion of some of the volatiles. The fluidised bed efficiency with coal and wood-pellets blend is lower than wood pellets alone possibly due to elutriation of coal char in the former two cases. Overall, efficiency decreases with increase in moisture content as fuel moisture consumes energy to evaporate and thus lesser energy is available to raise the temperature of the bed.

In the case of coal-pressed pulp blends, the efficiency at freeboard temperature is consistently higher than that at bed temperature as a result of overbed burning of volatiles from PP. The efficiency increases with increases in O_2 (%) in the flue gas (i.e the excess air level). Although the efficiency at bed temperature is relatively unaffected by excess air, that at freeboard temperature is increased by about 8% due to the effect of increased over bed burning with increase in excess air.

Small proportion of biomass can be co-fired with coal without drastically deteriorating the performance of combustion system. For example, no significant effect has been noted on the combustion performance of the fluidised bed test rig when 30% pressed pulp was mixed with coal due to very low dry mass contribution of biomass in this case.

9.2.4 Effect of Fuel Moisture on Throughput:

As mentioned earlier, air flow requirement at a fixed thermal input for a set bed temperature decreases with increases in fuel moisture content. The presence of moisture cools the bed as the moisture takes energy to evaporate and to raise its temperature to flue gas temperature so that with higher moisture content fuels, a specific bed temperature can be achieved at lower excess air levels (lower oxygen concentrations in the dry combustion products). For example, a bed temperature of 850 °C is achieved with 15%M blend at 11.7% O_2 (122% excess air) but with 55%M blend the temperature is achieved at around 10.2% O_2 (92% excess air) in the flue gas which is equivalent to 30% reduction in excess air.

During co-firing blends of coal and pressed pulp it is found that the reduction in air flow increases relatively sharply when PP proportion is increased to higher levels so that overall about 20% less air is required when the ratio of the pressed pulp is increased to 50%. Similarly, the air flow which is required to maintain a constant overbed temperature is progressively reduced as the proportion of the pressed pulp is increased to these high levels. The reductions in the required fluidising air flow rates will have a beneficial effect on the operation of the fluidised bed hot gas generator at Cantley since at present the flow rate of the fluidising gases and hence the amount of coal which can be burnt in the bed is limited by high pressure drops in the existing sparge pipe distributor. The ability to operate with lower excess air levels due to the cooling effect of the pulp will enable the thermal input to the full sized plant to be increased. Moreover, as the flue gas from the HGG is used to dry animal feed, the drying capacity of the combustion products will be increased by the presence of additional moisture, with a high specific heat, from the pressed pulp. However, there is a maximum limit on moisture content of flue gas used for drying. If temperature of the flue gas drops below its dew point along the drying path it would not evaporate any more moisture. Therefore, in order to make sure that the drying process is effective, temperature of the flue gas at the exit of the dryer should always be controlled at above its dew point.

9.2.5 NO_x Emissions:

The emissions of $NO_x$for all the solid fuels and combinations of fuels are found to be considerably higher than limits set out by EU Directive [EU Directive, 2010/75/EU], see Table 6.2. However, because of the research nature of the project, no control measures have been adopted as are used in the industry on full scale plants. The emissions of NO_x measured during Thoresby coal combustion tests correspond to a variation of fuel nitrogen conversion of about 24 – 32% over the experimental conditions tested with an average of 28% (converted to 6% O_2) based on the 1.62% nitrogen in Thoresby coal. Emissions of NO_x are not very much affected by temperature and tended to increase only slightly with bed temperature which suggests that thermal NO_x makes a very small contribution as would be expected at these bed temperatures, so that fuel NO_x is the dominant NO_x formation mechanism.

Emissions of NO_x decrease during co-firing due to lower nitrogen content of biomass. During all the tests NO_x emissions were found to be the highest for coal only firing and the lowest for wood pellets only firing, with their blend showing intermediate behaviour. Emissions of NO_x from the combustion of wood pellets are found to be almost 4.5 – 8 times lower than those from the coal. Moreover, the emissions of NO_x for 50/50 coal-pellets blend are almost half of those from coal and almost 2.3 times those from pellets. The emissions for coal-wood pellets blend are lower than coal-chips blends due to lower nitrogen content of the former. However the emissions for different coal-PP blends are relatively higher than coal-pellets and coal-chips blends due to very low proportion of combustible matter contributed by pressed pulp in the blends.

During co-firing of 50/50 blend of woody biomass with coal, effect of moisture on NO_x emissions was found to be negligible. Mass and thus volatiles contribution of high moisture biomass in a 50/50 blend with coal is lower than that from lower moisture biomass. Volatiles have the tendency to reduce NO_x emissions. Thus NO_x reduction ability of higher moisture biomass in a fixed blend proportion is reduced.

During co-firing coal with high moisture content biomass, coal nitrogen plays a dominant role due to lower nitrogen content and lower dry mass contribution of biomass. For example,

during coal and pressed pulp blends combustion nitrogen conversion is found to be almost the same as for coal alone due to domination of coal (dry mass basis) in the blend.

Increase in excess air increases oxygen level which creates favourable conditions for the oxidation of volatile nitrogen compounds. Lower excess air is required for higher moisture content fuels and therefore lower amount of oxygen is available to convert NH_3 to NO. Moreover, higher moisture fuels produce more O and OH radicals which form more NCO to convert NO to NO_2. However, overall effect of moisture on NO_x emissions during present study is found to be negligible due to the net effect of delayed ignition to increase NO_x and lower nitrogen content, lower temperatures and reactions on the char surface to decrease NO_x.

Emissions of NO_x increase with increase in bed temperature. At higher bed temperatures char is consumed more quickly and tendency of char to reduce NO_x is reduced. During co-firing the effect of temperature on NO_x is more significant because there is less char available in the bed due to relatively lower coal input and higher reactivity of biomass char. Fuels with higher volatiles to fixed carbon ratio tend to produce more NO_x due to lack of char in the bed to destroy NO_x and convert them to molecular nitrogen.

Measured emission of NO_x may have affected by point of measurement and may have been different to which could have been achieved if measured higher up in the freeboard region. However, it was not possible due to height restrictions caused by ceiling of the lab in which the fluidised bed rig was situated. Also, NO_x formation and destruction reactions are different for different fuels and at a particular point in the combustor emissions could have been different from optimum.

9.2.6 SO_2 Emissions:

The emissions of $SO_2$for all the solid fuels and combinations of fuels, except wood pellets, are found to be considerably higher than limits set out by EU Directive [EU Directive, 2010/75/EU], see Table 6.1. However, because of the research nature of the project, no control measures have been adapted as are used in the industry on full scale plants. Emissions of SO_2 are found to be the highest for coal and the lowest for pellets, with their blend

showing intermediate behaviour. The emissions for coal-pellets and coal-chips blends are higher than for pellets alone due to higher sulphur content of coal.

The emissions of SO_2 from Thoresby coal correspond to about 80 – 88% sulphur conversion on the basis of 1.5% sulphur in coal [British sugar]. These conversion efficiencies are reasonable taking into account sulphur trapped in the ash, the formation of SO_3 and uncertainties in the composition of coal. Emissions of SO_2 from combustion of 50/50 coal-pellets blend and pellets alone are found to be almost 2.5 times and 10 times lower than those from coal only combustion, respectively. Emissions of SO_2 with 50/50 blend are lower than the average value expected on the basis of coal and pellets alone firing. This can be attributed to the tendency of biomass to reduce SO_2 emissions and sulphur retention by biomass ash. During present work coal and biomass were fed above the bed and most of the volatiles could have been evolved in the freeboard region. In this case sulphur retention is reduced due to lesser contact with the bed material and ash.

Emissions of SO_2 increase slightly with increase in bed temperature. During present study it is found that SO_2 emissions increased slightly with increase in bed temperature for low moisture fuels e.g. coal, pellets and their blend. With higher moisture fuels e.g. coal-pulp blends effect of bed temperature on SO_2 emissions was more pronounced and the emissions found to be higher at higher bed temperatures.

It is not possible to comment on the effect of volatiles on SO_2 emissions for high moisture chips and pulp blends with coal due to influence of moisture on the emissions. Moreover, energy contribution of pressed pulp in the blends is very low 4.4 – 9.6%. Thus volatiles contribution of pulp in the blends is not significant and may have little effect, if any, on the emissions.

De-sulphurisation efficiency increases with increases in the amount of excess air. With coal and wood chips blends SO_2 emissions decreased with increase in excess air. The emissions with coal and 55% moisture wood chips blend are found to be 30% lower than coal and 15% moisture wood chips blend, although sulphur content of the former on dry mass basis is higher than the latter. This may be possibly due to conversion of SO_2 to H_2SO_4 by reaction

with water, due to production of more OH radicals at higher moisture contents. For details of the reaction please see section 6.6 of Chapter 6.

Emissions of SO_2 with coal-pressed sugar beet pulp blend are lower than those with coal alone and decrease with increase in proportion of pressed pulp in the blend due to increase in moisture content. If overall moisture content is kept constant, higher proportion of biomass in the blend results in lower SO_2 emissions due to lower sulphur content of biomass and higher sulphur retention by biomass ash. However, the results of emissions for different coal-pulp blends are interesting and vary considerably with change in blending ratio. The emissions decrease with increase in pulp proportion in the blend despite very little contribution of dry matter from pulp, possibly, due to increase in the moisture content and Ca/S ratio of the blend with increase in the pulp ratio. For similar moisture content and Ca/S ratio, SO_2 emissions tend to decrease with increase in biomass proportion.

9.2.7 CO Emissions:

The emissions of CO are found to be generally lower for coal than for pellets and 50/50 blend have shown an intermediate behaviour. This is possibly due to higher volatiles content of pellets which evolve and leave the bed unburned. This may also be the case with fine particles of char which could have been left the bed without burning at increased velocities and thus lower residence times. Emissions of CO from the combustion of coal and wood pellets blend are lower than those from coal and wood chips blend possibly due to relatively easier combustion of wood pellets.

During Thoresby coal combustion, CO emissions increase with increases in thermal input at a particular excess air level. For a particular thermal input, CO emissions first decrease with increases in excess air and then increase as excess air is further increased. Thus there is an optimum excess air at which CO emissions are at minimum. For the tests performed with Thoresby coal, wood pellets, 50/50 blend of Thoresby coal and wood pellets and 50/50 blend of Thoresby coal and wood chips of different moisture content during present work, CO emissions are found to be at the lowest at around 12 – 13.5% O_2 in the flue gas. With coal and pressed pulp blends air flow was lower and excess air did not reach to these levels.

Therefore it is not possible to comment on the oxygen level at which CO emissions could be at minimum during co-firing of coal and pressed pulp.

During coal-pulp blends CO emissions (normalised to 6% O_2) were found to be above 500 ppm for all the conditions tested. However, CO emissions found to be decreased with increase in pulp proportion in the blend despite increase in moisture. This is possibly due to delayed evolution of volatiles with increase in moisture. Increase in moisture results in increase in residence time and thus more time for the fuel to burn in the bed resulting in lower CO emissions. It may also be due to conversion of CO to CO_2 by water gas shift reaction.It could also be due higher CO reduction by increased OH radical produced at higher fuel moisture content. It was observed that influence of moisture on CO emissions was more pronounced at lower excess air levels. The emissions decrease with increase in excess air. With increase in excess air, difference in CO emissions was found to be lower at different moisture contents. At lower excess air levels, CO emissions are higher due to higher wet oxidation of char at elevated moisture.

9.2.8 Agglomeration:

Experimental data proved that calculation of agglomeration indices for unknown fuels is a good way to pre-assess their behavior before combustion in fluidised beds. Muffle furnace tests of different blends of sand and fuel at different controlled temperatures for a set period of time are also good indicators of the behavior of fuels during combustion in a fluidised bed. During muffle furnace tests of vinasse and sand blendwith fresh sand being used each time, no clinker was found in the test samples when tested at 800 °C. Observations show that there was no clinker found when vinasse content in the sample was increased up to 20%. When vinasse content was increase beyond 20%, sample started ignition. First signs of clinker were found at 30% vinasse in the sample but the clinker was easily breakable. However, during top up tests to simulate continuous combustion process, hard agglomerates were observed after 2 hours and 20 minutes with total amount of vinasse added was 84g (74% of the total material added). However, results of muffle furnace tests cannot be directly compared with fluidised bed tests due to different dynamic conditions but they can be used to pre-assess potential fuels. During muffle furnace tests with blends of raffinate and sand it was observed that the

sample turned to a hard lump when ratio of raffinate in the blend was 50% due to higher alkali content of raffinate.

Accumulative effect of vinasse top up and prolonged test time resulted in the formation of hard agglomerates. It was concluded that soft agglomerates found during first few top up tests were hardened as more vinasse was added and subjected to high temperature for prolonged period. The agglomerates also observed to be grew in size as the tests progressed and eventually after 3 hours and 20 minutes and with 80% vinasse in total material, all the material turned into a bigger, hardened lump.

Behavior of different fuels during experiments on fluidised bed test rig proved that agglomeration behavior of fuels can be predicted using agglomeration indices. Not only the length of the test but also the amount of alkali present in biomass influences agglomeration conditions and biomass having higher potassium content tends to form harder agglomerates relatively quickly. Agglomerates formed at higher temperature tend to lose and break up as the temperature is lowered. Molten phase solidifies and push of the air can break the loosely bonded lump particles down to individual particles. Therefore, higher fluidising velocities may be able to extend operational times. Agglomerates formed in the earlier stages of fluidised bed firing tend to harden and turn to unbreakable as subjected to high temperatures for a period of time.

Higher char particle temperatures or hot spots can initiate agglomeration phenomenon locally which then extends throughout the bed due to the fact that the agglomerates act as nuclei to attract other particles to form bigger agglomerates.

Coal mineral matter particularly calcium helps preventing agglomeration and increases operational time. For example, during natural gas-raffinate co-firing bed slumped quickly, in lesser time and with lesser amount of raffinate feeding into the bed as compared to coal-raffinate co-firing. This indicates that lime can be used as a bed material to increase operational times while firing these troublesome fuels.

The study found that feed rate of alkali into the bed is very important. Higher the amount of alkali per unit time fed into the bed, higher the chances of agglomeration to occur.

Introduction of small amount of alkali into fluidised bed for a longer time is better than introducing larger amount in a shorter time.

Agglomeration is unlikely to be major problem when firing pressed pulp particularly when size degradation of the sand during long term operation is taken into account. Therefore, PP can be used as fuel in fluidised bed without the use of alkali getters as long as operational parameters are properly controlled. However, alkalis, particularly Potassium, tend to accumulate in the bed overtime and may be problematic in the long run even when burning fuels having relatively low levels of them. During co-firing alkalis behave differently depending upon their origin and parent compound. However, vinasse and raffinate can't be used without adapting measures such as addition of alkali getters to reduce agglomeration.

9.2.9 Water injection:

During steady state tests with water injection, there is little evidence found that the water gas reaction results in higher CO or hydrogen emissions even at the higher temperatures where the effect would be most significant. During water injection, CO emissions thought to increase due to reduction in the effective mixing of air and volatile and reduced diffusion of air into the coal. Emissions of NO_x remained the same before and after water injection which again justified the arguments that the NO_x emissions are not affected by moisture in fuel.

At higher water to coal mass ratios it is difficult or even impossible to maintain bed temperature due to higher amount of energy being used to evaporate water. Drop in bed temperature due to water injection can be compensated by reducing air flow. The higher the water to coal ratio, the lower the air flow required to get the same bed temperature. Therefore, keeping air flow constant more coal can be fed into the bed to get the same bed temperature if water in injected. However, in the case of water injection emissions of CO may be up to 10 times higher than those without water injection. At increased coal input, volatiles are released in larger amount and may have left the bed unburned. Secondary air may be used to burn the unburned fuel in the freeboard.

During water injection tests with coal it is observed that CO emissions are high ($\geq$500 ppm) only at bed temperatures below about 750°C. This temperature is well below that associated

with the water gas reaction which suggests that high CO levels are caused by incomplete combustion of volatiles or reaction of water with char. The temperature is also much lower than the operating temperatures at Cantley so that it appears that the generation of high levels of carbon monoxide and hydrogen are unlikely on the full scale plant.

Thus, it can be concluded that cooling effect of injected water may be able to make it possible to achieve full capacity of 40 MW of the HGG of British Sugar's Cantley factory. Although it is found that water injection into the bed enhances throughput by around 20%, no effort has been made to quantify the relationship between increased amounts of coal input with increase in injected water flow. The amount of water which can be injected into fluidised bed is dictated, firstly, by the limit of optimal bed temperature achievable to sustain stable combustion (combination of effective radiation, convection and conduction heat transfer). Secondly, while the overly excess air is being gradually displaced the overall air-fuel ratio reduces and this should not be in any case reduced to less than the optimal value required for complete combustion. This optimal air/fuel ratio is likely to be higher with water injection due to the possible reasons of poorer mixing of air and volatile and reduced diffusion of air into coal.

9.3 Overall Conclusion:

Overall, it can be concluded from this technical study and a parallel financial analysis, that there are significant benefits in co-firing pressed sugar beet pulp with coal. Consequently it is recommended that a full scale trial should be considered for the large fluidised bed hot gas generator at British Sugar. Alternatively, initially it should be possible to carry out a simpler full scale water injection test to achieve bed cooling.

9.4 Future Recommendations:

Co-firing of biomass with coal is a preferred option due to a number of reasons. Sustainable supply of fuel is not an issue as in case of biomass shortage plant can be switched to 100% main fuel. Calorific value of biomass fuels, particularly of those having high moisture content, is usually low and can be compensated by co-firing it with a fuel of high calorific

value. Plants designed for coal firing can be adapted with relative ease for co-firing up to a certain percentage of biomass in blend with coal.

Despite considerable efforts have been made, there are still several challenges to the large scale biomass combustion and co-firing i.e. sustainable supply of fuel, uniformity in the characteristics of fuel, combustion chemistry, corrosion caused by biomass impurities, ash deposition, effect on efficiency due to high moisture content of biomass fuels.

Depending upon the results and observation of present study following recommendation for future work can be made. The recommendations have been classified as general and specific depending upon their importance in relevance to HGG at Cantley site of British Sugar.

9.4.1 General Recommendations:

a) Oxy-Fuel Combustion:

During co-firing tests of blends of Thoresby coal with pressed sugar beet pulp, maximum proportion of pulp in the blend which was able to sustain combustion was found to be 50%. Above this proportion, temperatures in the bed were too low to sustain the combustion process. In order to successfully fire higher proportion of high moisture biomass in coal-biomass blend, oxygen enhanced or oxy-fuel combustion can be employed. Oxy-fuel combustion, combustion in oxygen rather than in air, gives higher flame temperatures due to elimination of nitrogen of air which acts as diluting agent to lower flame temperature. However, elimination of nitrogen will result in reduced fluidising velocities due to reduction in overall volumetric flow of the oxidizer. In order to increase this flow flue gas, after clean up, need to be recycled back to the bed. There should be an optimum recycle ratio at which fluidising velocity can be maintained and also fluidised bed can tolerate maximum proportion of high moisture biomass. Research is needed to assess the feasibility of such a process and its economic implications.

Oxyfuel combustion will result in increasing in dry mass contribution of biomass in blends and may lead to results and observations different to those mentioned in this thesis. Moreover, oxyfuel combustion is one of the competing carbon capture technologies which isa

hot issue in the world due to its implications on climate change. Therefore, application of oxyfuel combustion to high moisture biomass fuel combustion in fluidised beds will result in killing two birds in one stone.

b) Secondary air:

Secondary air can be used to provide more flexibility to the system. The use of secondary air can make it possible to adjust primary air flow keeping overall air to fuel ratio constant. Split between primary and secondary air also affects operational parameters such as fluidising velocity, bed temperatures etc. Therefore, adjustment of primary and secondary air streams to get optimal performance will be critical.

Emissions of CO can be controlled by adjusting air to fuel ratio and by proper mixing of air and fuel by employing secondary air. Flexibility in the adjustment of primary air may result in lower CO emissions due to better control. Use of secondary air can result in reduced CO emissions by burning unburned volatiles and fine char in the freeboard. However, decrease in the amount of primary air results in increase in SO_2 emissions. Thus split of air between primary and secondary needs to be balanced for optimum system performance.

9.4.2 Specific Recommendations:

a) Water injection:

Main aim of this work was to assess the possibility of occurrence of water gas shift reaction, therefore, no effort has been made to find out upper and lower limits of water flow rate into the bed. Further research need to be carried out in order to fully assess the effects of water injection on fluidised bed and to determine feasible upper and lower water injection limits. Furthermore, tests should be carried out to assess the behavior/response of full scale fluidised bed, hot gas generator of Cantley, to water injection.

It is found that CO emissions increase when water is injected into the bed. The emissions can arise from incomplete combustion, reaction of water with char or reverse water gas reaction. During this study no effort has been made to quantify the origin of CO from different

sources. Further research is needed to fully assess and quantify formation potential of CO from these mechanisms. However, it is found that CO emissions by water gas shift reaction are not significant.

Air requirement for maintaining a fixed bed temperature decreases when water is introduced into the bed fired at a fixed power input. Thus, in order to maintain a fixed bed temperature at a fixed air flow rate, more coal can be introduced into the bed when the bed is cooled by water injection. It is found that throughput of the fluidised bed rig can be enhanced by 20% by water injection. However, relationship between increased amounts of coal input at a certain amount of water injection is not established. Further research is needed to establish this relationship.

b) Feeding Biomass into the Bed:

Because biomass fuels have higher reactivity in comparison to coal, they should be fed into the bed, not onto the bed. This will help in increasing the amount of biomass being burnt in the bed and less in the freeboard. At Cantley, the HGG has existing arrangements which can be used to feed pressed sugar beet pulp from the bottom of the bed through sparge pipes. However, due to sticky nature of the pressed pulp, there is a danger of choking the pipes and thus deteriorating the efficiency of the HGG. Therefore, it is recommended to perform a full scientific investigation in order to assess the effect of feeding pressed pulp through the sparge pipes.

During co-firing coal and pressed sugar beet pulp, emissions of SO_2 were observed to be lower and were thought to be due to lack of contact time between coal ash and biomass sulphur as the blend was fed on the top of the bed. Feeding of biomass into the bed may help reducing SO_2 emissions by retaining more sulphur in the bed by Ca in coal ash.

c) Separate Coal and Biomass feeding:

Some of the data acquired during the tests was scattered possibly due to poor mixing of two fuels in a blend. The mixing problem could arise from different bulk densities and thus energy densities of fuels in blends. During present study the fuels were mixed first and then

loaded into the feed hopper, as explained in Chapter 3, where also are highlighted issues which could result into poor mixing of two fuels in blends and thus may result in variations in the coal and biomass feed ratios. Therefore, it is recommended that separate feeders for coal and biomass should be used to minimise this problem. This will also provide better control on operation and will be less labour intensive.

d) Particle size analysis:

During fluidised bed combustion, particles of bed tend to increase in size due to deposits of sticky materials, particularly potassium, on their surfaces. The buildup of surface layer can lead to particles bigger enough in size to effect fluidising velocities and ultimately can result in defluidisation of the bed. Therefore, particle size distribution analyses need to be carried out in order to find out rate of deposits formation. Sieve analysis, optical granulometry, X-Ray diffraction or laser diffraction are some of the techniques which can be employed for this purpose. Inherently, particles of bed tend to shatter after some time due to collision. Thus, particle size distribution analyses need to be carried out frequently, after every few hours, to see the effect of deposit build up on the surface of the particles.

e) More research for fate of Potassium:

It has been observed that the amount of potassium accumulated in the bed, for raffinate and vinasse tests, is very much higher than the amount of potassium introduced into the bed. This shows discrepancy in the SEM results. However, it is possible that the distribution of potassium in the bed was not even. As the samples were taken from the top of the bed it is possible that this has higher potassium content as compared to the bottom. However, this theory violates the inherent nature of fluidised bed to distribute material fed into the bed equally throughout the bed. The results indicate that more research is needed to fully understand the behaviour of potassium present in fuels combusted in fluidised beds.

During co-firing coal and pressed sugar beet pulp for agglomeration assessment, potassium accumulation was observed in the successive samples. However a safe level for the potassium content cannot be predicted so that much longer timescale tests is recommended for a definitive conclusion.

f) Full Scale tests:

Thermal input of the test rig used for the study is around 2000 times lower than that of the HGG at Cantley. Therefore, the results obtained from this study can't be extrapolated to the scale of HGG as there is huge capacity gap. However, the results of the present study have made it clear that it is possible to co-fire pressed pulp in a fluidised bed with very low agglomeration tendency. The fluidised bed (HGG) at Cantley is not operated in a same way as the test rig. Due to difference in size, number of coal feed points and air flow inlets, HGG may have different flow dynamics. Therefore, it is recommended that to fully assess the behavior of pressed pulp combustion in the HGG full scale tests need to be carried out. It may be feasible to perform tests on a fluidised bed of pilot scale size, of the order of 100 kW, before testing HGG. If proved successful, the trials can be extended to HGG.

Moreover, as explained in Chapter 6, NO_x and SO_2 emissions data measured during the tests is considerably higher than the emissions limits set out in European Directive, see Tables 6.1 and 6.2. Therefore, it is necessary to perform full scale trials on full scale plant using emission control measures to establish feasibility and environmental compatibility of co-firing pressed sugar beet pulp with coal in fluidised bed hot gas generator of British Sugar, Cantley site.

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Appendix A: Typical Proximate, Ultimate and Ash analysis of biomass fuels

Table A1: Comparison of proximate and ultimate analysis

	Dry Vinasse[1]	Begasse[1]	Begasse[5]	Begasse[3]	Coal[1]	AB coal[2]	Bit.[5] Coal	HVB[6] coal	MVB[6] coal	MSW[2]	SBC[3]	Rice[4] husk	Dry[6] sludge
Proximate													
Fixed carbon	11.73	6.1	18.35	12.11	16-93	n.a	34.5	41.2	56.2	n.a	47.6	13.2	5.5
Volatile matter	69.31	40.2	n.a.	65.24	3-50	31.2	n.a.	39.2	26.3	69-71	38	74	72.9
Ultimate													
C	39.72	23.8	23.5	49.66	50-95	75	44.14	78.1	85.9	35.4-39	73.2	42.3	62.8
H	8.6	2.8	3.25	5.71	2-5.5	4.8	3.23	6.3	4.9	4.9	5.1	6.1	6.9
O	n.a	20.1	21.75	41.08	2-4	10-12	11.58	13.4	7	31.9-33.9	7.9	37.5	16.8
S	0.12	Trace	0	0.03	0.5-7	0.7	0.59	1	0.5	0.2	3	0.04	1.7
N	1.65	Trace	0	0.21	0.5-3	1.3	0.91	1.3	1.7	0.6	0.9	1.1	5.4
Cl												0.2	
Ash	18.95	1.7	1.5	2.65	2-3	8.5-10	34	14.3	15	23-25	9.4	12.8	21.6
Moisture	0	52	50	20	0	0.7	5.55	5.3	2.5	35	5	9.4	0
Heating value MJ/kg				19.04		29.6				8.4	30.84	16.3	

[1]Cortez and Perez (1997)
[2]Desroches-Ducarne *et al.*, (1998) AB = American Bituminous (results are on dry ash free basis)
[3] Santos, (2004) SBC = Sub-bituminous coal (results are on wet basis)
[4]Armesto, (2002)
[5]Narayanan and Natarajan (2006)
[6]Shimizu *et al* (2007)
Table A1: Comparison of proximate and ultimate analysis (continued)

	Vegetable waste[7]	MSW dry[7]	Olive oil waste[8]	Wood chips[5]	Cane trash[5]	SA[6] coal	Lignite coal[5]	Polish coal[9]	Cerejon coal[9]	Straw[9] pellets	MBM[9]		
Proximate													
Fixed carbon		4	15.12	38.11	38.27	73.1	22.69	55.9	50.4	17.8	5.6		
Volatile matter		63	80			12		33.1	37	75.3	55.9		
Ultimate													
C	19.2	35.81	13.3	48.8	49	92.3	29.06	72.9	66.4	45.9	33.3		
H	2.56	4.82	2.7	6.37	5.89	3.5	2.35	5	5.9	6.9	5.2		
O	15.04	24.43	22.7	44.4	43.36	3.5	12.31						
S	0.16	0.41	-	0	0	0.2	0.5	0.5	1	<0.2	0.4		
N	1.04	0.78	0.3	0	0	1.5	0.28	1.3	1.4	0.7	8.5		
Cl								0.26	0.07	0.27	0.29		
Ash	2	0.8	2	0.37	1.75	12.8	7	11	12.6	6.9	38.5		
Moisture	60	32.2	59	7	4	2.1	48.5	4.7	9.3	9.1	3.2		
Heating value MJ/kg								29.2	27.8	16.3	14.4		

[1]Cortez and Perez (1997)
[2]Desroches-Ducarne *et al.*, (1998) AB = American Bituminous (results are on dry ash free basis)
[3] Santos, (2004) SBC = Sub-bituminous coal (results are on wet basis)
[4]Armesto, (2002)
[5]Narayanan and Natarajan (2006)
[6]Shimizu *et al* (2007) SA = semi-anthracite
[7]Suksankraisorn *et al.* (2003)
[8]Cliffe and Patumsawad (2001)
[9]Helena Lopes *et al* (2007)

Table A1: Comparison of proximate and ultimate analysis (continued)

	Bit. Coal (polish)[1]	Wood chips[1]	Sewage sludge[1]	Sawdust cypress[2]	Sawdust hemlock[2]	Sawdust spruce[2]	Wood bark[3]	Dewatered sewage sludge[3]	Wheat straw[4]	Greenhouse residue[4]	Olive cake pellets[4]
Proximate											
Fixed carbon	-	-	-	10.5	21.8	12.4	14.5	7	21.5	5.5	15.7
Volatile matter	35.3	82	91.1	72.9	65.9	76.9	25	10.1	77.9	61	64.2
Ultimate											
C	82.5	50.6	53.2	51.6	51.8	50.4	51.8	38.8	56.7	47.1	42.1
H	5	6.3	7.1	6.2	6.2	6.3	7.7	5.7	6.7	7.4	5
O	9.9	43	30.6	40.4	40.6	41.6	29.4	21.6	48.8	10.9	31
S	0.9	0.02	1.9	0.46	0.38	0.34	0.89	1.2	0.2	<0.1	0.1
N	1.7	0.14	7.1	0.65	0.6	0.62	8.9	6.5	1	1	1.3
Cl	0.07	0.01	0.05	-	-	-	-	-	-	0.1	0.3
Ash	15.7	0.8	42.1	0.7	0.4	0.7	0.4	26.6	68	32	8.2
Moisture	8.7	40.8	15.9	15.9	11.9	10	60.1	56.3	13.9	2.5	11.9
Heating value MJ/kg	24.2	10.2	9.4	-	-	-	-	-	-		

[1]Leckner and Lyngfelt (2001)
[2]Li *et al.* (2004)
[3]Velden *et al.* (2007)
[4]Khan *et al.* (2008)

Table A1: Comparison of proximate and ultimate analysis (continued)

	Bituminous coal[1]	Demolition wood pellets[1]	Wood pellets (Pine)1	Pepper plant residue1	Sunflower pellets1	Sewage sludge1	Coal[2] (Columbia)	Wood bark[2]	Sludge[2]
Proximate									
Fixed carbon	48.1	19.7	14.5	19.5	19.5	7	44 – 45.7	5.3 – 8.4	5.3 – 8.4
Volatile matter	32.3	69.9	80.4	60.5	65.2	44.6	31.3 – 31.6	30.1 – 35.6	21.4 – 28.5
Ultimate									
C	65.7	45.5	45.5	33.8	44.1	52	60.1 – 62.1	17.8 – 22.3	10.3 – 15.7
H	5.6	6.6	6.6	4	5.17	6.3	4.22 – 4.25	1.11 – 2.72	1.39 – 2.09
O	7.7	47.7	47.7	39.1	34.6	32.1	8.92 – 8.97	16.42 – 18.8	12.7 – 15.13
S	0.5	<0.1	-	0.5	0.1	3.1	0.58 – 0.59	0.02 – 0.05	0.05 – 0.06
N	1.2	0.9	-	2.5	0.5	6.3	1.26 – 1.35	0.04 – 0.17	0.05 – 0.09
Cl	-	0.1	-	0.1	0.1	-	0.02 – 0.04	0.01	0.01 – 0.02
Ash	14.7	1.7	0.2	13.5	4.1	41.5	7.7 – 9.2	0.2 – 0.3	7 – 22.9
Moisture	4.9	9.1	4.9	6.5	11.2	6.9	15.1 – 15.8	55.7 – 64.4	52.6 – 60
Heating value MJ/kg	-	-	-	-	-	-	24.8 – 25.6	6.93 – 9.53	3.27 – 6.11

[1]Khan *et al.* (2008)
[2]Van de Velden *et al.* (2007)

Table A1: Comparison of proximate and ultimate analysis (continued)

	Hard coal[1]	Brown coal[1]	Straw[1]	Miscanthus[1]	Wood[1] (Beech)	Sewage[1] sludge			
Proximate									
Fixed carbon	57.1	42.83	19.9	17	16.5	6.6			
Volatile matter	34.7	52.11	74.4	78.2	83.2	45.9			
Ultimate									
C	72.48	65.9	47.4	50.7	48.7	24.4			
H	5.64	4.9	4.5	4.4	5.7	4.3			
O	11.1	23	40.4	39.1	45	19			
S	0.94	0.39	0.05 – 0.11	0.04 – 0.26	<0.05	0.94			
N	1.28	0.69	0.4 – 0.8	0.08 – 0.51	0.13	3.54			
Cl	0.128	<0.1	0.4 – 0.73	0.15 – 0.25	<0.01	-			
Ash	8.25	5.1	6.1	4.9	0.34	47.5			
Moisture	2.8	10.4	10.6	7.6	-	3.6			
Heating value MJ/kg	30.14	23.2	17.09	18.01	30.1	10.51			

[1]Spliethoff and Hein (1998), Heating value on dry basis

Table A2: Ash Analysis:

	Rice[1] husk	Brown coal[2]	Bituminous coal[2]	Straw[2]	Hard coal[3]	Brown coal[3]	Straw[3]	Miscanthus[3]	Wood[3] (Beech)	Sewage[3] sludge
SiO_2 (%)	87.7	6.99	70.2	59.6	43.7	9.5	56.2	70.6	15.2	38.3
K_2O (%)	5.4	0.63	1	12	3.22	-	23.7	12.8	8.6	2.19
P_2O_5 (%)	3.7	0.03	-	3.5	0.27	-	4.4	39.1	45	19
CaO (%)	1.3	37.95	1.3	12.5	5.8	41	6.5	7.5	37.3	9.1
MgO (%)	0.8	16.51	0.5	0.8	3.8	14	3	2.5	8.5	2.8
Na_2O (%)	0.2	2.73	0.3	0.8	0.86	22	1.3	0.17	2	2.21
Fe_2O_3 (%)	0.1	14.52	6.7	0.4	10.2	15	1.2	1	3.8	12.5
Al_2O_3	-	4.29	17.1	0.5	24.7	5	1.2	1.1	2.65	14.8
TiO_2	-	-	-	-	0.97	-	0.06	0.06	0.26	0.8
SO_3 (%)	-	15.28	I	2.1	5.7	13.5	1.1	1.7	3	2.21
Cl	-	0.46	-	3.88	-	-	-	-	-	-
Cr (ppm)	560	-	-	-	-	-	-	-	-	-
Zn (ppm)	603	-	-	-	-	-	-	-	-	-

[1]Armesto, *et al.*, (2002)
[2]Arvelakis and Frandsen, (2007)
[3]Spliethoff and Hein (1998)

Table A2: Ash Analysis (Continued):

	Wood pellets[1]	Demolition wood pellets[1]	Pepper plant residue[1]	Greenhouse residue[1]	Sunflower pellets[1]	Olive cake pellets[1]	Wheat straw[1]	Sewage sludge[1]	Bituminous coal[1]	Vinasse[2]
SiO_2 (%)	4.3	20.4	12.6	28.4	2.9	12.8	53.1	38.3	59.7	1.51
K_2O (%)	16.8	10.5	24.6	9.7	22.8	47.9	30	2.2	2.3	10.73
P_2O_5 (%)	3.9	11.1	5.2	3.8	15.2	6	4.1	15.4	0.1	0.168
CaO (%)	55.9	27.5	32.2	25.8	21.6	17.5	17.7	9.1	1.8	3.52
MgO (%)	8.5	7.5	7.4	5.7	21.6	4.9	3	2.8	1.9	1.63
Na_2O (%)	0.6	4.8	0.9	0.8	0.24	3.9	4.5	2.2	1	1.04
Fe_2O_3 (%)	1.5	2.2	2	18.4	0.8	3	1.2	12.5	7	0.69
Al_2O_3 (%)	1.3	3.5	4.9	3.9	0.6	2.9	3.6	0.8	20.3	-
SO_3 (%)	1.3	-	-	-	14	1.1	-	1.1	1.3	4.36
Cl	-	-	-	-	-	-	-	-	-	3.79
Cr (ppm)	-	-	-	-	-	-	-	-	-	-
Zn (ppm)	-	-	-	-	-	-	-	-	-	0.115
Mn (%)	5.9	0.3	0.2	0.3	0.1	0.1	-	-	<0.01	

[1]Khan *et al.* (2008)

[2]Sheehan and Greenfield (1980); raw material was molasses

Appendix B: Typical Characteristics of Natural gas, Gas oil and Span 80

Table B1: Natural gas composition

Constituents	Percentage
CH_4	94.4
C_2H_6	3
C_3H_8	0.5
C_4H_{10}	0.2
C_5H_{12}	0.1
C_6H_{14}	0.1
CO_2	0.2
N_2	1.5
M. Wt.	17.01
CV (MJ/m^3) at 15 °C and 1 atm	34.9
Density STP (kg/m^3)	0.76

Table B2: Average properties of Gas oil [Spiers, 1932]

Composition C %	86.3
H %	12.8
S %	0.9
Sp. Gr. : D (15.5 °C/15.5 °C)	0.87
Kinematic viscosity: C.G.S. units at 32 °F	0.108
Boiling range °C	177
Vapour pressure mmHg at 50 °C	2.6
Equation for vapour pressure	
Log p = A – B/T A	7.05
T = abs. temp. (°C) B	2135
Mean specific heat between 0	

and 100 °C (cal/g/°C)	0.485
Combustion: air requirements per kg of fuel kg dry air m^3	14.4
Calorific Value: cal/gram gross net	10980 10310
Flashpoint: (Pensky-Martin) °F	168
Spontaneous ignition temperature in oxygen (°C)	272

Table B3: Properties of Span 80

Chemical Formula	$C_{24}H_{44}O_6$
Physical state	Liquid
M. Wt.	428.61
Colour	Amber, Yellow
Boiling Point	>100 °C
Specific gravity	1

Appendix C: Fluidised Bed Efficiency calculation method

So called "Fluidised Bed Efficiency" is defined as the efficiency of the fluidised bed to produce hot combustion products to be used in the subsequent drying process.

The efficiency is calculated at two different locations i.e. bed and freeboard. To calculate the efficiency energy content of the flue gas is calculated based on the bed temperature (BT) and the freeboard temperature (FBT_1) measured at 0.24m above the static bed.

The Efficiency is then calculated by the following equation.

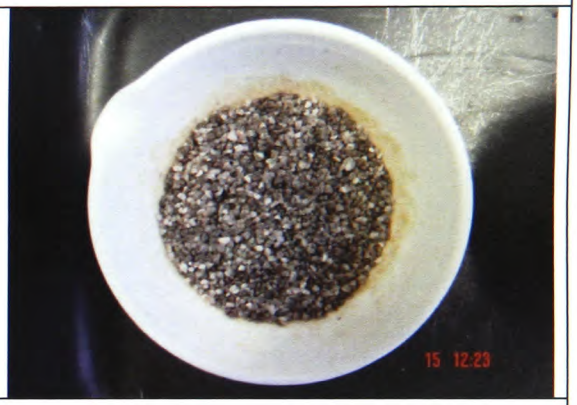
$$\text{Efficiency at BT} = \frac{\text{Flue gas energy content at BT}}{\text{Energy input}} \text{ X } 100$$

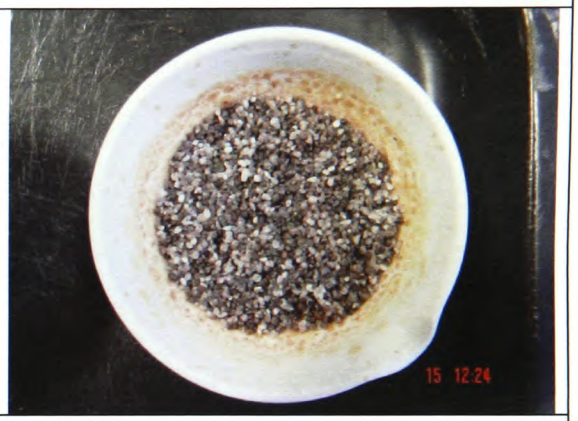
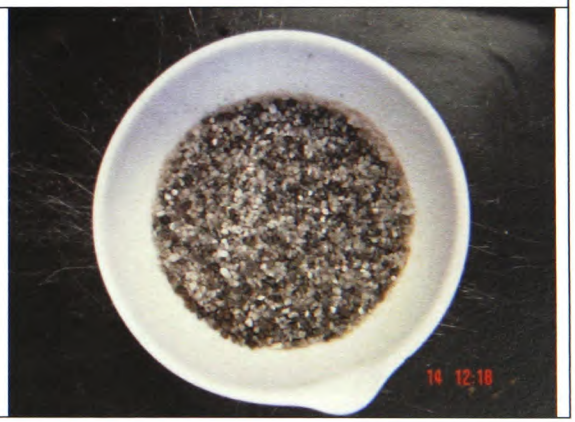
$$\text{Efficiency at } FBT_1 = \frac{\text{(Flue gas energy content at FBT1+A)}}{\text{Energy input}} \text{ X } 100$$

Where, A = Energy loss through the walls of the containment tube between BT and FBT_1 measurement points. The loss is calculated based on the natural gas experiments as explained in Chapter 4 and is found to be on average 1.5 kW.

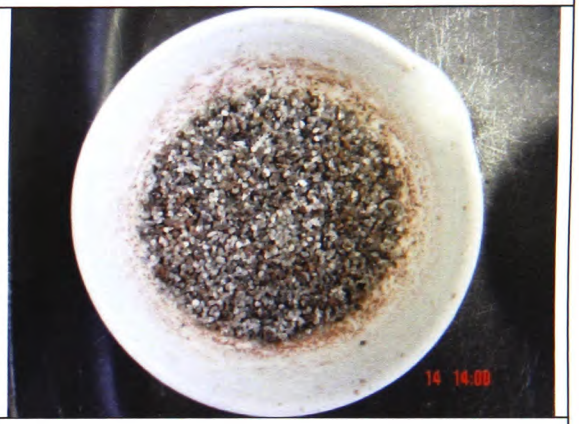
Appendix D: Muffle furnace Tests of Blends of Vinasse and Raffinate with Sand

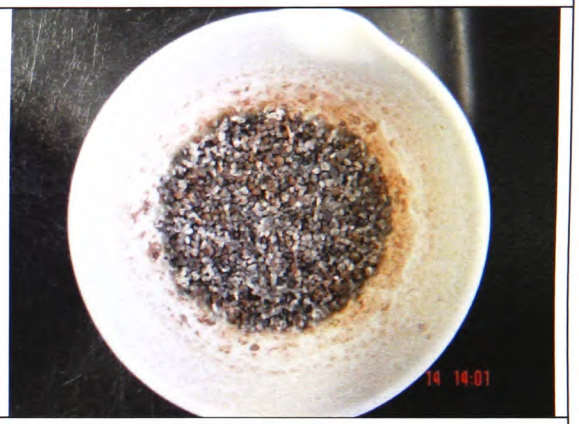
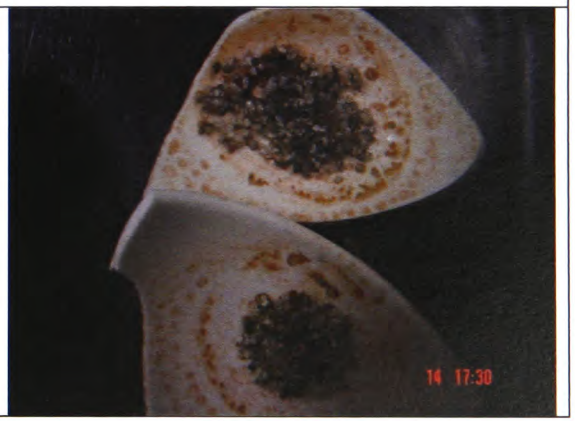
Test 1: Muffle furnace Tests with varying Blends of Vinasse and Sand at 800 and 850 °C

Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	60	8% / 3.198g	92% / 36.804g	40.002g	36.502g	3.500g	8.75%	Surface less stiff seconds after being taken out from the furnace. Extremely easy to separate when cooled down to room temperature.	
850°C	60	10% / 4.015g	90% / 35.987g	40.002g	35.830g	4.172g	10.43%	No clinker can be found although sample hardness was not tested when still hot (temperature almost identical to furnace temperature seconds after the sample was removed from the furnace).	

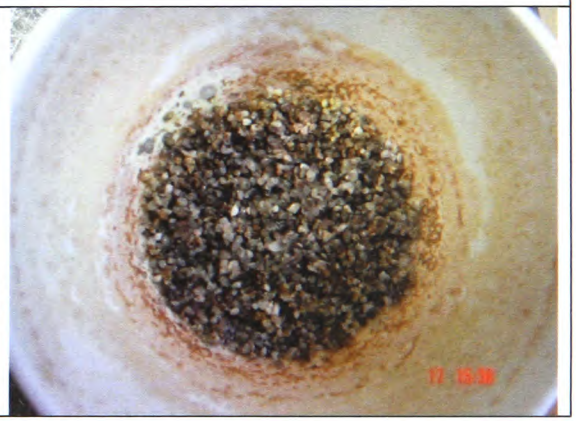
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	60	12% / 4.798g	88% / 35.203g	40.001g	35.089g	4.912g	12.28%	Surface slightly rigid than the 8% Vinasses sample when still hot but can be separated using a sharp object. Easily separated when cooled down to room temperature.	
850°C	60	14% / 5.603g	86% / 34.402g	40.005g	34.290g	5.715g	14.29%	Mostly unclinkered when cooled down to room temperature. Sample hardness was not tested when still hot but believed to be less firm than the following tests.	

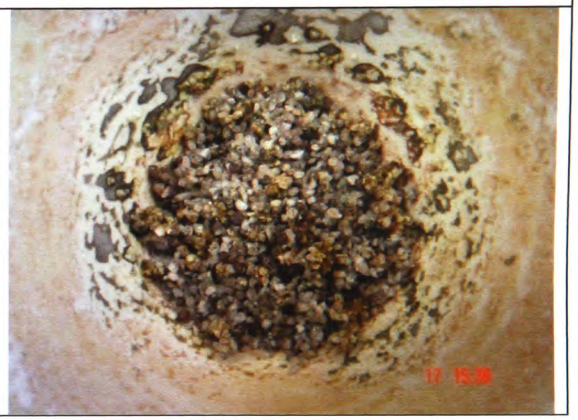
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	60	16.7% / 6.685g	83.3% / 33.320g	40.005g	33.338g	6.667g	16.67%	The surface was hard seconds after being taken out from the furnace but mostly unclinkered when cooled down to room temperature.	
850°C	60	20% / 8.012g	80% / 31.996g	40.008g	32.100g	7.908g	19.77%	The surface was hard when just being removed from the furnace but mostly unclinkered when cooled down to room temperature.	

Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	60	25%/10.005g	75% / 30.001g	40.006g	30.245g	9.761g	24.40%	Sample was ignited when first put into the furnace. Surface was hard when just being removed from the furnace but mostly unclinkered after being cooled down to room temperature.	
850°C	60	30% / 11.999g	70% / 28.017g	40.016g	28.358g	11.658g	29.13%	Fire can be seen when first put into the furnace. Surface was hard when still hot and clinkered can be noticed but can easily be separated when cooled down to room temperature.	

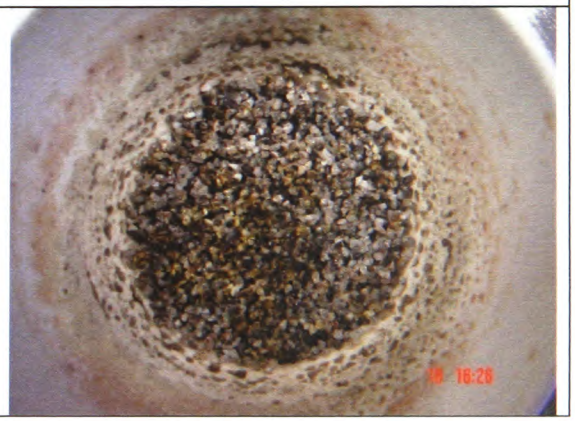
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	60	50% / 20.010g	50% / 20.000g	40.010g	20.206g	19.804g	49.50%	Fire was intense when first put into the furnace and overflow of Vinasses was observed. Surface was hard when still hot but can easily be separated when cooled down to room temperature.	
850°C	60	75% / 30.012g	25% / 9.995g	40.007g	N/A	N/A	N/A	Fire was intense when first put into the furnace and broke the crucible. Not many samples left but clinkered was harden when cooled down to room temperature but can still be separated.	

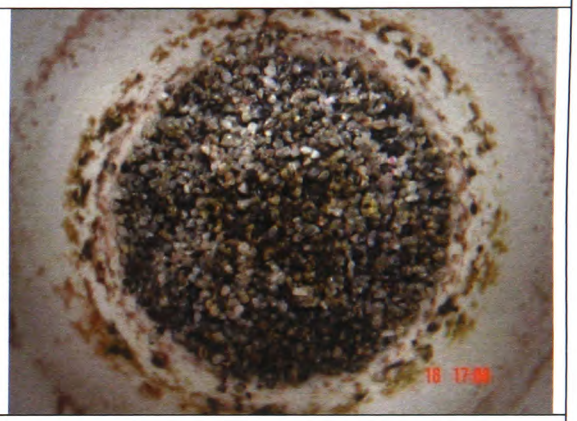
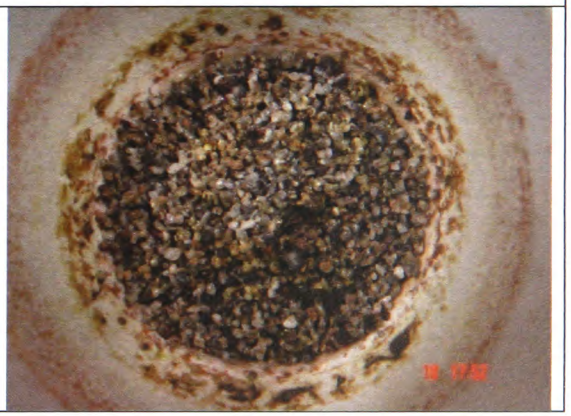
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
800°C	60	0% / 0g	100% / 39.998g	39.998g	39.660g	0.338g	0.85%	Sand has been discoloured to mostly red.	
850°C	60	0% / 0g	100% / 40.000g	40.000g	39.540g	0.460g	1.15%	As with 800°C, sand has been discoloured to mostly red.	

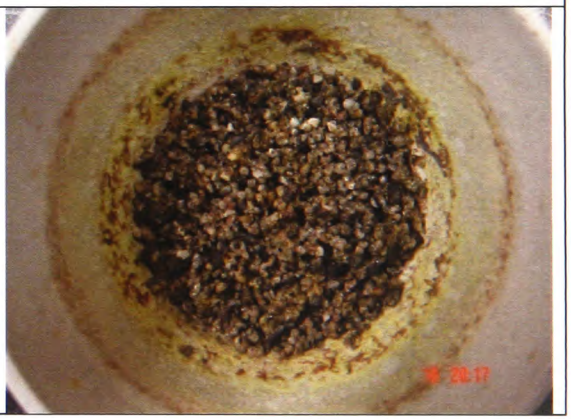
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
800°C	60	20% / 7.998g	80% / 32.000g	39.998	32.065g	7.933g	19.83%	The surface was hard seconds after being taken out from the furnace but can easily be separated even still hot. Mostly un-clinkered when cooled down to room temperature.	
800°C	60	30% / 12.002g	70% / 27.998g	40.000g	28.278g	11.722g	29.31%	Not much different to the 20%/80% mix. Surface was hard when still hot but can be easily separated when cooled down to room temperature.	

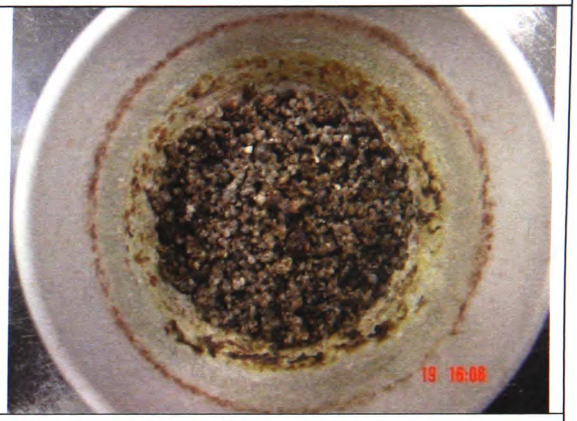
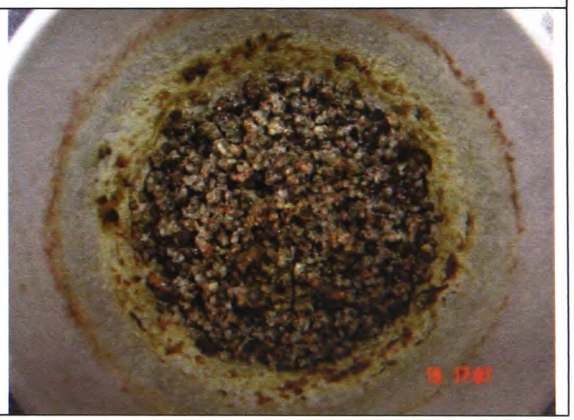
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
800°C	60	50% / 20.001g	50% / 20.000g	40.001g	20.873g	19.128g	47.82%	Surface was hard when still hot. Mostly un-clinkered but some clinkers became harder & unbreakable even cooled down to room temperature.	

Test 2: Top-up Tests with Vinasse and Sand at 850^0 C in Muffle Furnace

Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	20	30% / 11.998g	70% / 28.005g	40.003g	28.312g	11.691g	29.23%	Mostly un-clinkered when cooled down to room temperature. (Top-up 1)	N/A
850°C	20	30%/12.004g	70% / 28.312g	40.316g	28.998g	11.318g	28.07%	Surface became harder when still hot but can easily be separated when cooled down to room temperature. (Top-up 2)	

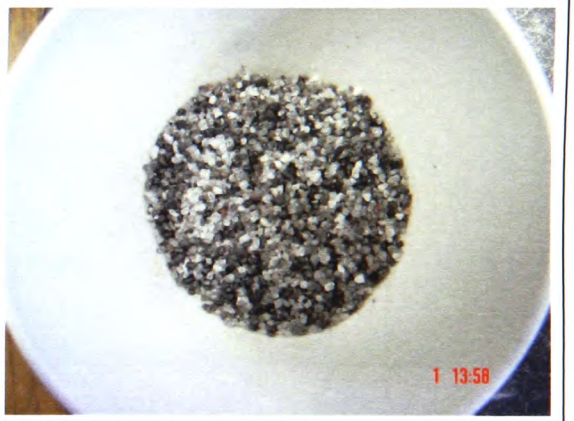
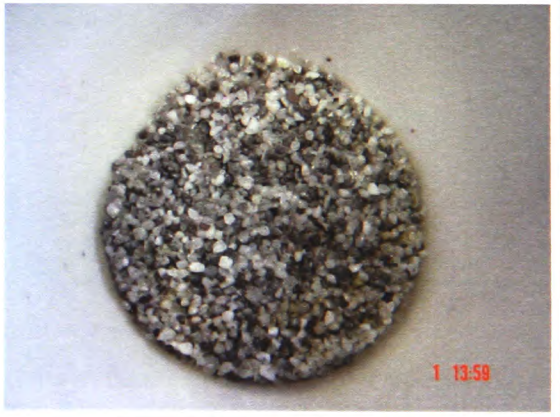
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	20	30% / 12.001g	70% / 28.998g	40.999g	29.617g	11.382g	27.76%	Sand has been discoloured to mostly dark grey after being added 30% of Vinasses for 3 consecutive times. (Top-up 3)	
850°C	20	30% / 12.000g	70% / 29.617g	41.617g	30.240g	11.377g	27.34%	Surface was hard seconds after being removed from the furnace. The amount of clinker began to form increased. (Top-up 4)	

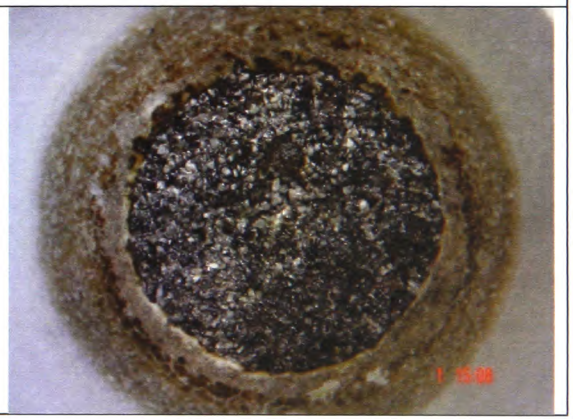
Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	20	30% / 12.000g	70% / 30.240g	42.240g	30.869g	11.371g	26.92%	Surface was harder when still hot but can still be separated. More clinkers can be seen after being cooled down to room temperature. (Top-up 5)	
850°C	20	30% / 12.000g	70% / 30.869g	42.869g	31.446g	11.423g	26.65%	Sand can be separated with extra force after being cooled down to room temperature but more clinkers can be noticed. (Top-up 6)	

Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	20	30% / 12.000g	70% / 31.446g	43.446g	32.052g	11.394g	26.23%	Very difficult to separate when cooled down to room temperature. More clinkers were formed. (Top-up 7)	
850°C	20	30% / 12.000g	70% / 32.052g	44.052g	32.710g	11.342g	25.75%	Very hard to separate the sample even with considerable force. Clinkers were getting bigger. (Top-up 8)	

Furnace Temp (°C)	Duration (minutes)	% of Vinasses (%) / Weight of Vinasses (g)	% of Sand (%) / Weight of Sand (g)	Weight of Vinasses + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	20	30% / 12.000g	70% / 32.710g	44.710g	33.307g	11.403g	25.50%	Extremely difficult to separate the sample even after being cooled down to room temperature. (Top-up 9)	
850°C	20	30% / 12.000g	70% / 33.307g	45.307g	33.891g	11.416g	25.20%	Large lump of clinker was eventually form and extremely hard to separate even after being cooled down to room temperature. (Top-up 10)	

Test 3: Muffle furnace Tests with varying Blends of Raffinate and Sand at 850^0 C

Furnace Temp (°C)	Duration (minutes)	% of Raffinate (%) / Weight of Raffinate (g)	% of Sand (%) / Weight of Sand (g)	Weight of Raffinate + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	60	7% / 2.800g	93% / 37.202g	40.002g	37.365g	2.637g	6.60%	Sand has been discoloured to white and grey. Surface was slightly hard seconds after being removed from the furnace but can easily be separated when cooled down to room temperature.	
850°C	60	14% / 5.600g	86% / 34.402g	40.002g	34.987g	5.015g	12.54%	Sand has been discoloured to white and grey. Surface was hard when still hot. After being cooled down to room temperature, extra force was needed to separate the sample.	

Furnace Temp (°C)	Duration (minutes)	% of Raffinate (%) / Weight of Raffinate (g)	% of Sand (%) / Weight of Sand (g)	Weight of Raffinate + Sand (g)	Weight (after furnace) (g)	Mass Loss (g)	% of Mass Loss (%)	Remarks	Sample Image
850°C	60	25% / 10.000g	75% / 30.005g	40.005g	31.242g	8.763g	21.90%	Surface was extremely hard when still hot. Extra force was applied to separate the sample after being cooled down to room temperature.	
850°C	60	50% / 20.000g	50% / 20.000g	40.000g	22.405g	17.595g	43.99%	Surface was extremely hard and unbreakable even cooled down to room temperature. No change at all of re-fluidisation.	

Appendix E: Results of SEM analysis of bed material

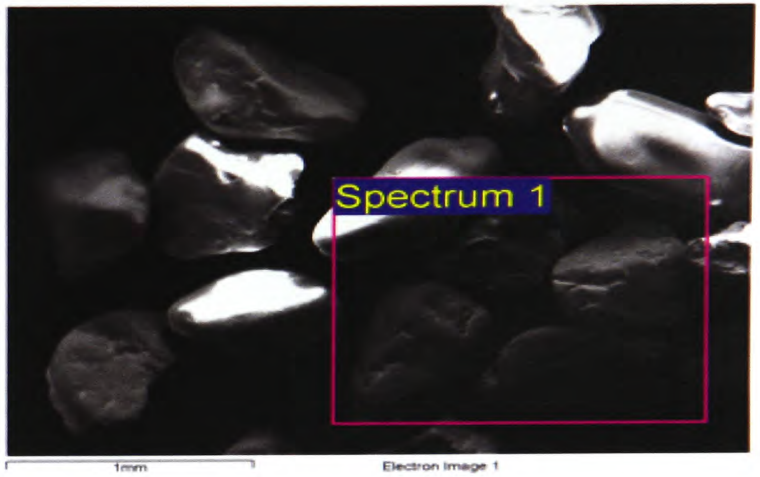
E1: SEM results of Sand

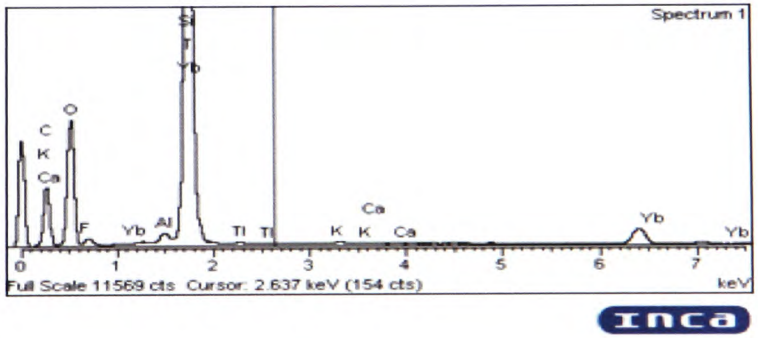
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 7

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Yb YbF3 1-Jun-1999 12:00 AM
Tl Not defined 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	38.44	49.20
O K	40.85	39.26
F K	1.28	1.04
Al K	0.24	0.14
Si K	18.81	10.30
K K	0.09	0.03
Ca K	0.05	0.02
Yb L	0.02	0.00
Tl M	0.21	0.02
Totals	100.00	





Comment:

E2: SEM results of Coal Sample 1

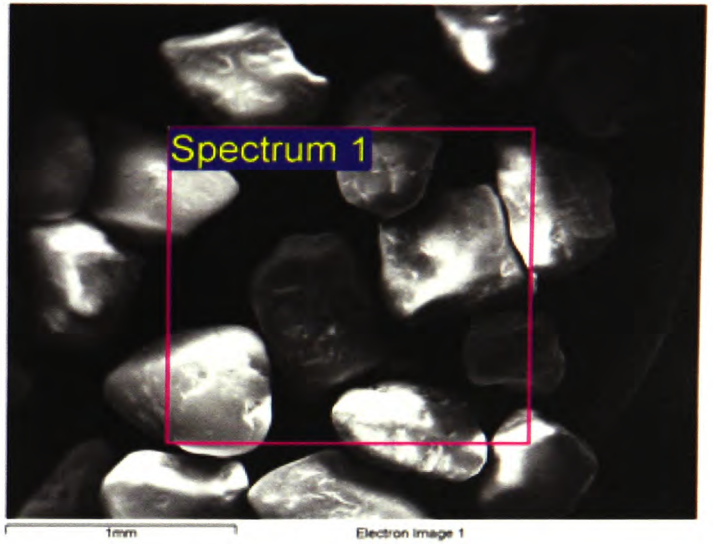
Spectrum processing :
Peaks possibly omitted : 6.404, 7.058 keV

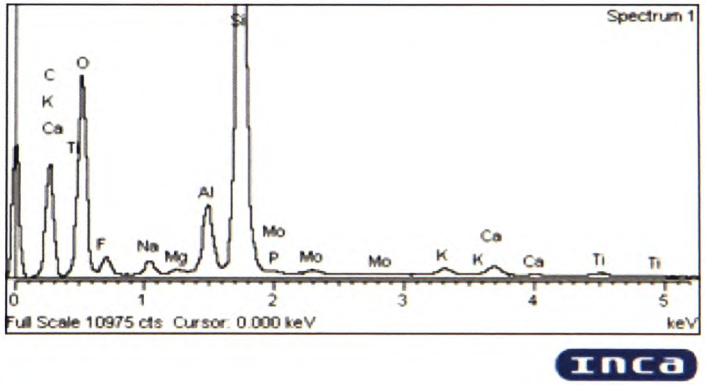
Processing option : All elements analyzed (Normalised)
Number of iterations = 7

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Mo Mo 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	37.89	47.98
O K	43.78	41.61
F K	2.24	1.79
Na K	0.78	0.52
Mg K	0.12	0.08
Al K	1.82	1.03
Si K	12.31	6.67
P K	0.06	0.03
K K	0.21	0.08
Ca K	0.31	0.12
Ti K	0.15	0.05
Mo L	0.33	0.05
Totals	100.00	

Comment:
Sample3 26012010





E3: SEM results of Coal Sample 2

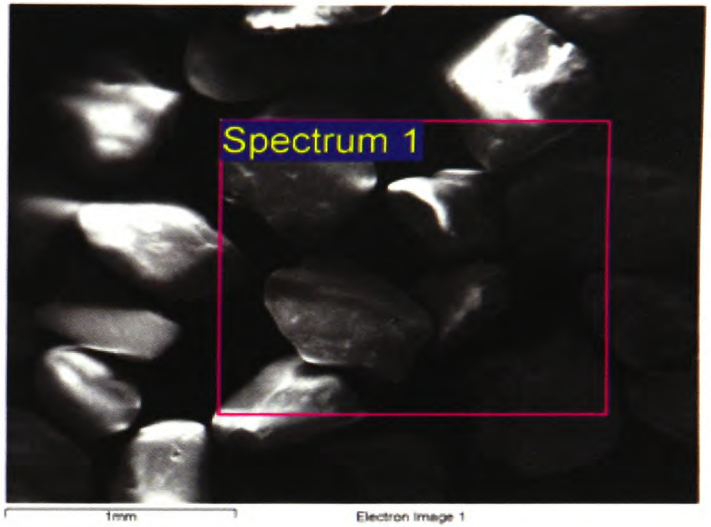
Spectrum processing :
Peaks possibly omitted : 6.403, 7.061 keV

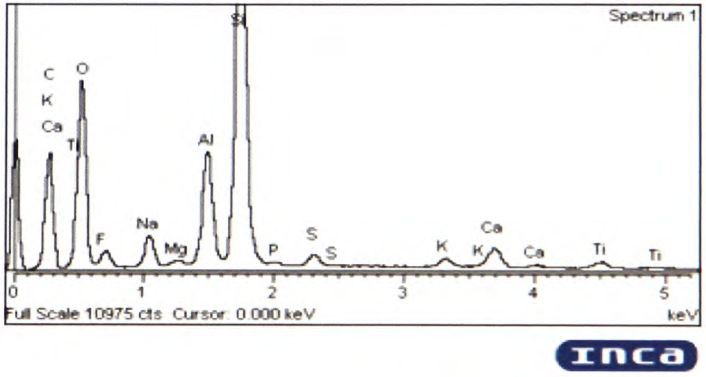
Processing option : All elements analyzed (Normalised)
Number of iterations = 7

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	38.87	49.24
O K	41.67	39.63
F K	2.08	1.67
Na K	1.74	1.15
Mg K	0.15	0.10
Al K	3.06	1.73
Si K	10.73	5.81
P K	0.09	0.04
S K	0.35	0.16
K K	0.27	0.10
Ca K	0.69	0.26
Ti K	0.31	0.10
Totals	100.00	

Comment:
Sample4 26012010





E4: SEM results of Coal Sample 3

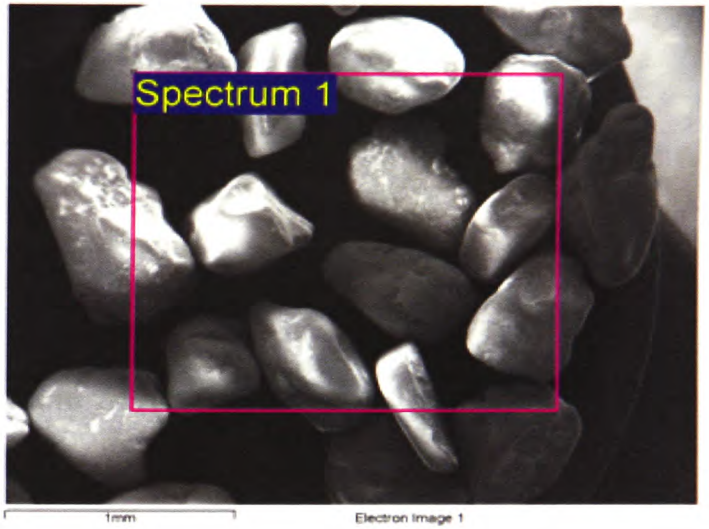
Spectrum processing :
Peaks possibly omitted : 6.403, 7.055 keV

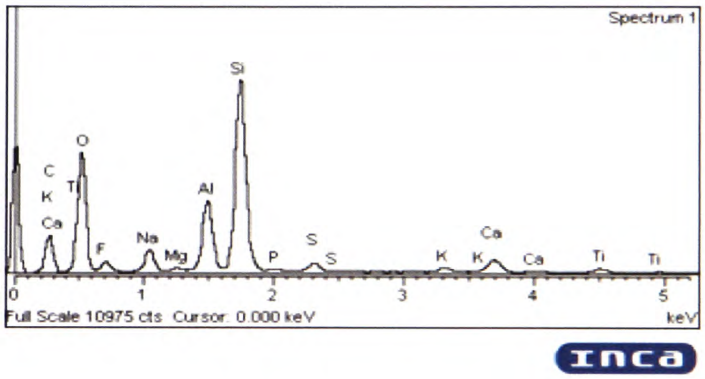
Processing option : All elements analyzed (Normalised)
Number of iterations = 7

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	29.16	38.69
O K	47.12	46.94
F K	2.95	2.48
Na K	2.67	1.85
Mg K	0.14	0.09
Al K	4.16	2.45
Si K	11.51	6.53
P K	0.11	0.06
S K	0.53	0.26
K K	0.29	0.12
Ca K	0.96	0.38
Ti K	0.41	0.14
Totals	100.00	

Comment:
Sample 5 26012010





E5: SEM results of Coal-Pulp Sample 1

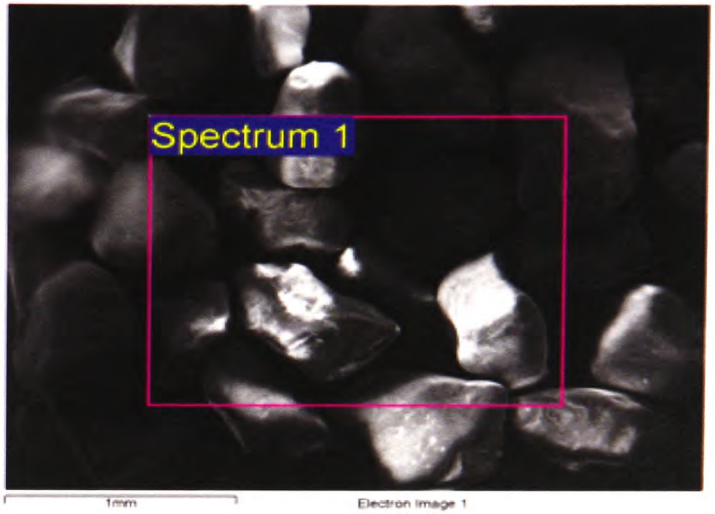
Spectrum processing :
Peaks possibly omitted : 6.402, 7.058 keV

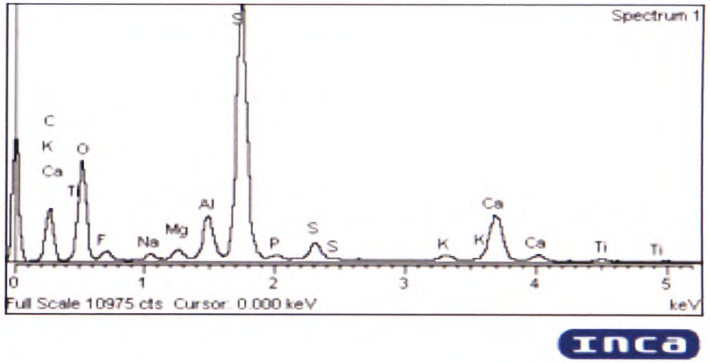
Processing option : All elements analyzed (Normalised)
Number of iterations = 7

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	35.16	45.99
O K	41.93	41.17
F K	2.08	1.72
Na K	0.60	0.41
Mg K	0.61	0.40
Al K	2.08	1.21
Si K	12.62	7.06
P K	0.26	0.13
S K	0.98	0.48
K K	0.32	0.13
Ca K	3.15	1.24
Ti K	0.22	0.07
Totals	100.00	

Comment:
Sample6 26012010





E6: SEM results of Coal-Pulp Sample 2

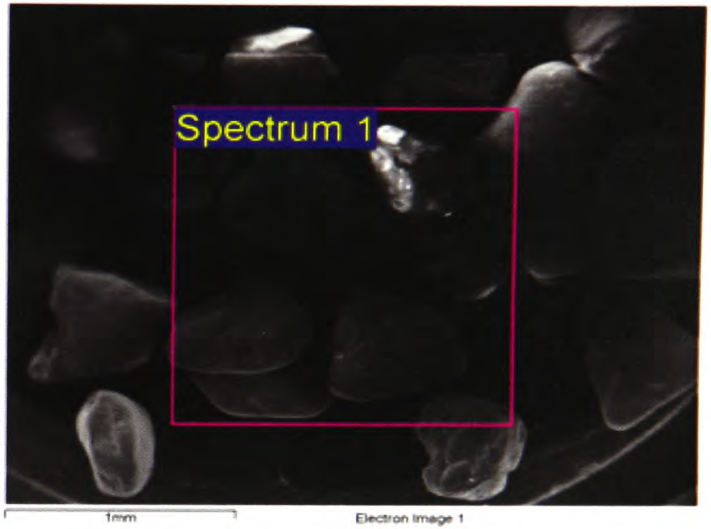
Spectrum processing :
No peaks omitted

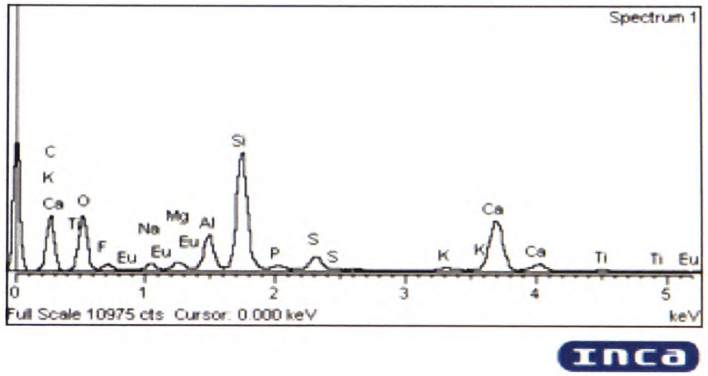
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Eu EuF3 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	42.03	53.62
O K	37.26	35.69
F K	1.37	1.11
Na K	0.84	0.56
Mg K	0.70	0.44
Al K	2.34	1.33
Si K	8.30	4.53
P K	0.32	0.16
S K	1.08	0.52
K K	0.18	0.07
Ca K	4.80	1.83
Ti K	0.28	0.09
Eu L	0.49	0.05
Totals	100.00	

Comment:
Sample7 26012010





E7: SEM results of Coal-Pulp Sample 3

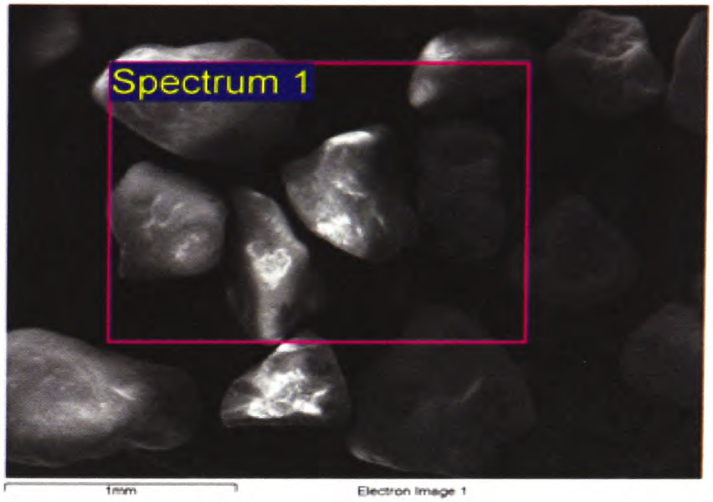
Spectrum processing :
Peaks possibly omitted : 5.430, 6.402, 7.063 keV

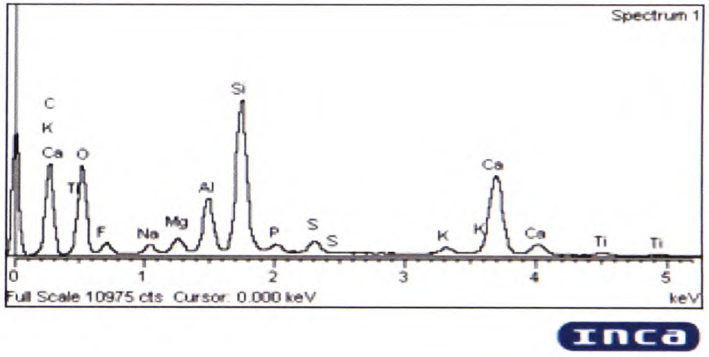
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	41.75	52.84
O K	38.88	36.94
F K	1.82	1.45
Na K	0.83	0.55
Mg K	0.82	0.51
Al K	2.50	1.41
Si K	6.98	3.78
P K	0.40	0.20
S K	0.59	0.28
K K	0.30	0.12
Ca K	4.87	1.85
Ti K	0.25	0.08
Totals	100.00	

Comment:
Sample 8 26012010





E8: SEM results of Coal-Pulp Sample 4

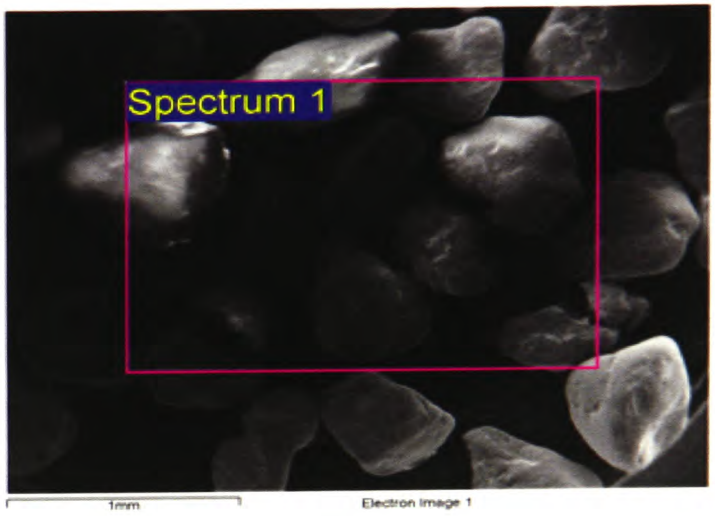
Spectrum processing :
Peaks possibly omitted : 5.435, 6.402, 7.057 keV

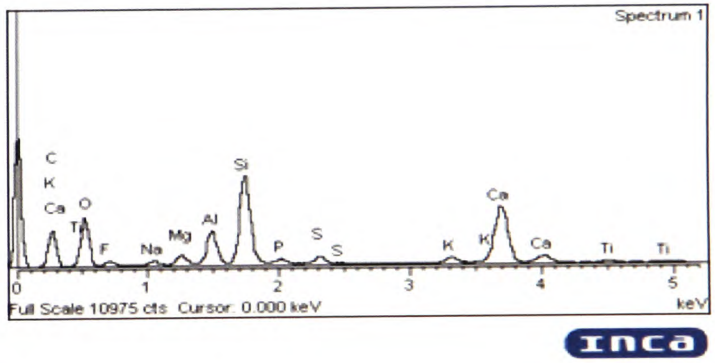
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	36.28	47.72
O K	40.15	39.64
F K	1.84	1.53
Na K	0.81	0.56
Mg K	1.12	0.73
Al K	2.95	1.73
Si K	8.04	4.52
P K	0.44	0.23
S K	0.65	0.32
K K	0.56	0.23
Ca K	6.80	2.68
Ti K	0.35	0.11
Totals	100.00	

Comment:
Sample9 26012010





E9: SEM results of Coal-Pulp Sample 5

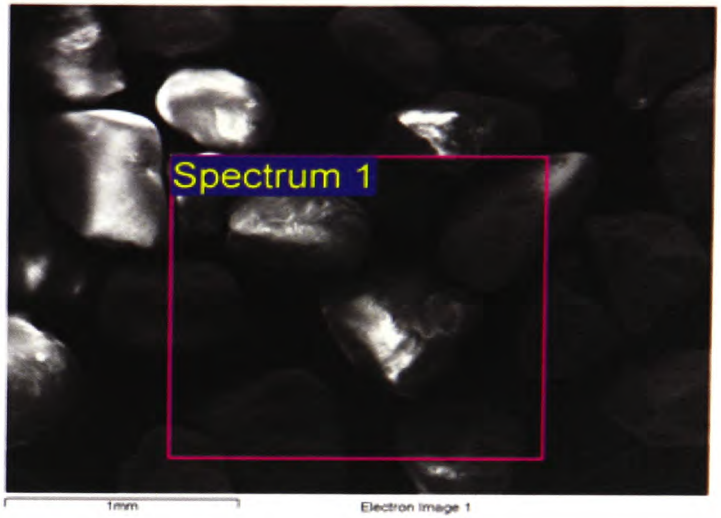
Spectrum processing :
Peaks possibly omitted : 6.404, 7.058 keV

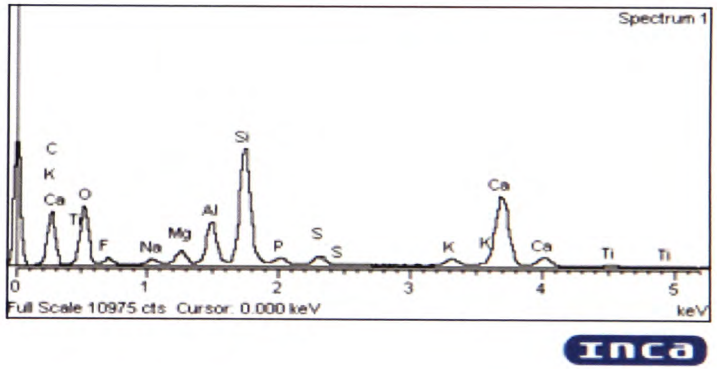
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	38.94	50.54
O K	38.33	37.35
F K	1.90	1.56
Na K	0.65	0.44
Mg K	1.11	0.71
Al K	2.85	1.65
Si K	8.03	4.46
P K	0.46	0.23
S K	0.60	0.29
K K	0.50	0.20
Ca K	6.37	2.48
Ti K	0.25	0.08
Totals	100.00	

Comment:
Sample 10 26012010





E10: SEM results of Coal-Pulp Sample 6

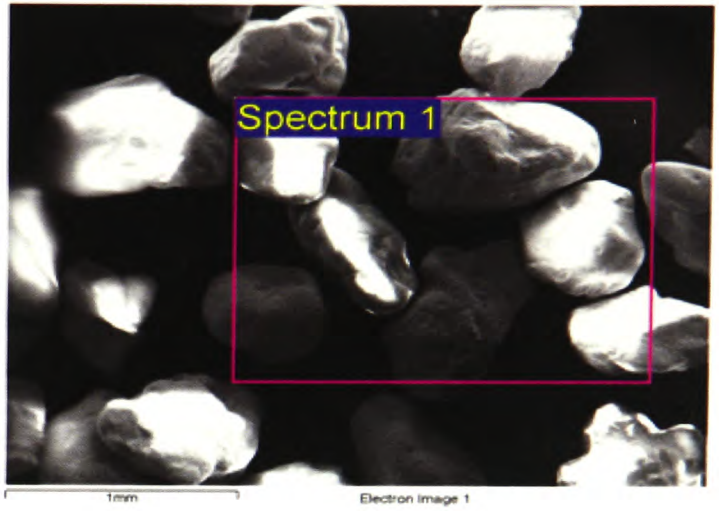
Spectrum processing :
Peaks possibly omitted : 6.402, 7.059 keV

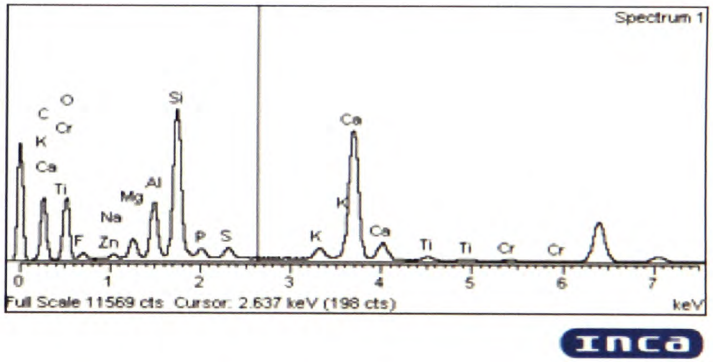
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Cr Cr 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	37.97	50.67
O K	34.69	34.76
F K	2.53	2.13
Na K	0.43	0.30
Mg K	1.32	0.87
Al K	3.07	1.83
Si K	8.11	4.63
P K	0.60	0.31
S K	0.58	0.29
K K	0.69	0.28
Ca K	9.26	3.70
Ti K	0.39	0.13
Cr K	0.15	0.05
Zn K	0.21	0.05

Comment:
Sample 11 280110





E11: SEM results of Coal-Pulp Sample 7

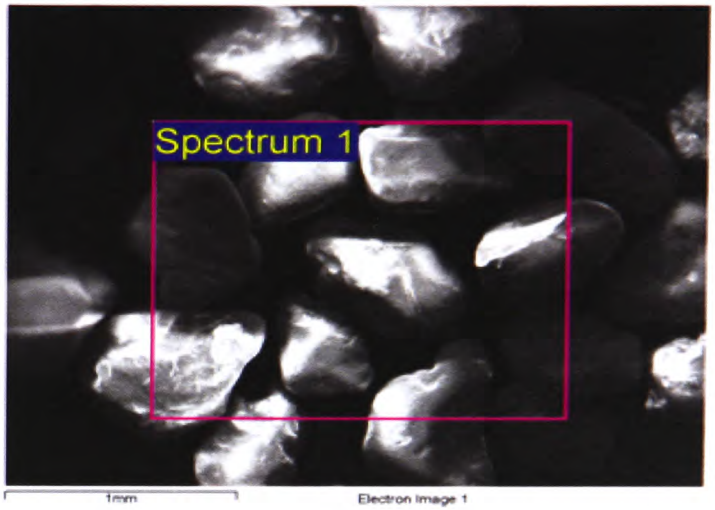
Spectrum processing :
No peaks omitted

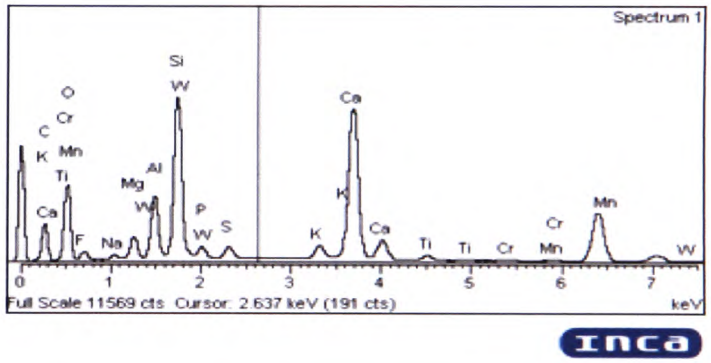
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Cr Cr 1-Jun-1999 12:00 AM
Mn Mn 1-Jun-1999 12:00 AM
W W 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	27.41	39.15
O K	39.73	42.60
F K	2.59	2.34
Na K	0.43	0.32
Mg K	1.65	1.16
Al K	3.56	2.26
Si K	9.34	5.71
P K	0.74	0.41
S K	0.73	0.39
K K	0.85	0.37
Ca K	11.54	4.94
Ti K	0.49	0.17
Cr K	0.18	0.06
Mn K	0.17	0.05

Comment:
Sample 12_080210





E12: SEM results of Coal-Pulp Sample 8

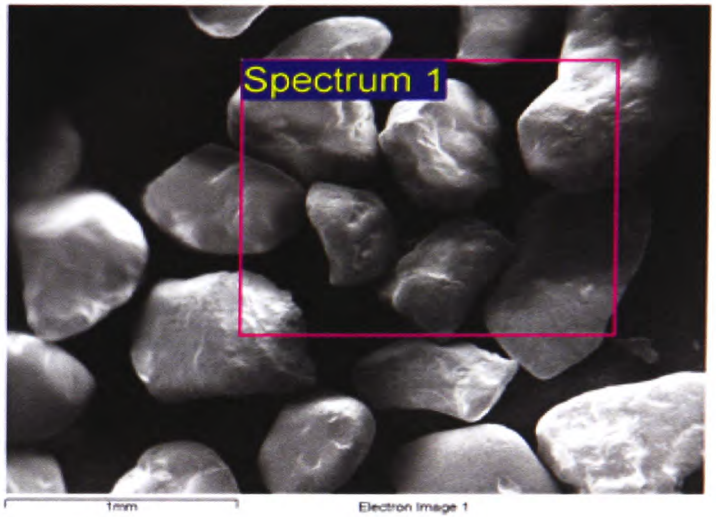
Spectrum processing :
Peaks possibly omitted : 7.055, 7.490, 12.440, 18.495 keV

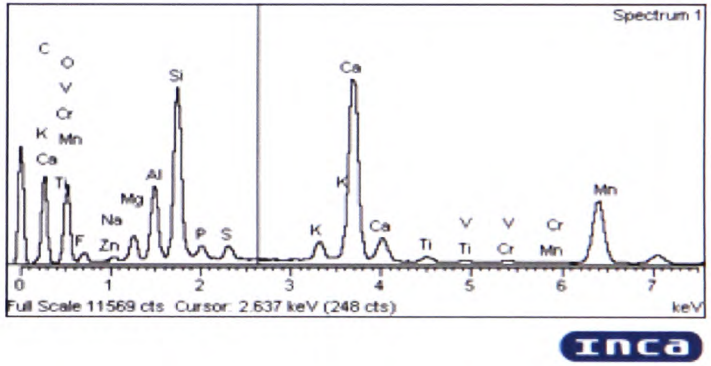
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
V V 1-Jun-1999 12:00 AM
Cr Cr 1-Jun-1999 12:00 AM
Mn Mn 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	52.80	57.53
O K	44.35	36.28
F K	1.81	1.24
Na K	0.43	0.24
Mg K	1.70	0.92
Al K	3.90	1.89
Si K	9.15	4.26
P K	0.82	0.35
S K	0.85	0.35
K K	1.08	0.36
Ca K	13.17	4.30
Ti K	0.50	0.14
V L	-31.14	-8.00

Comment:
Sample 13_100210





E13: SEM results of Coal-Raffinate Sample 1(top of bed)

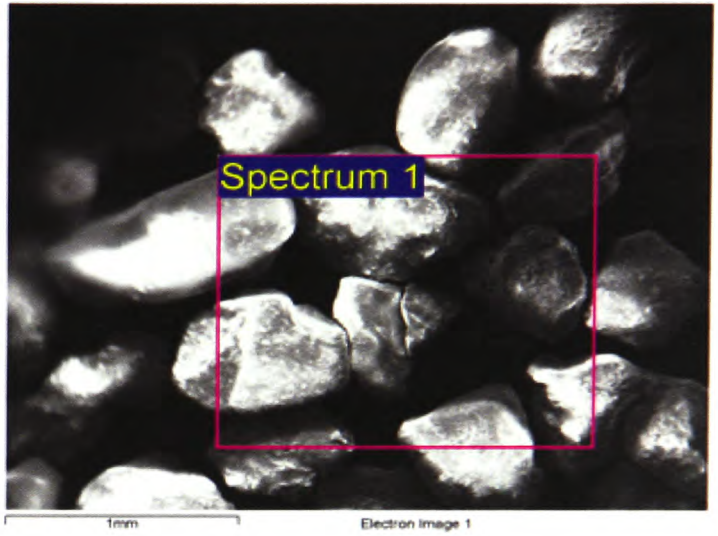
Spectrum processing :
Peaks possibly omitted : 4.034, 6.402, 7.056, 8.665 keV

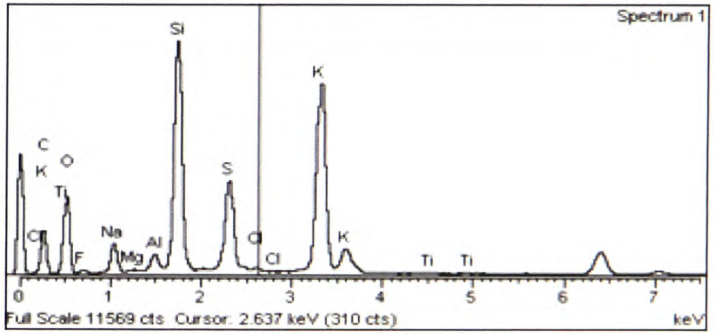
Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	30.88	43.48
O K	36.76	38.86
F K	0.72	0.64
Na K	2.92	2.15
Mg K	0.10	0.07
Al K	0.70	0.44
Si K	10.72	6.45
S K	4.86	2.56
Cl K	0.21	0.10
K K	12.05	5.21
Ti K	0.09	0.03
Totals	100.00	

Comment:
Sample 15 110210





E14: SEM results of Coal-Raffinate Sample 2 (agglomerated lump)

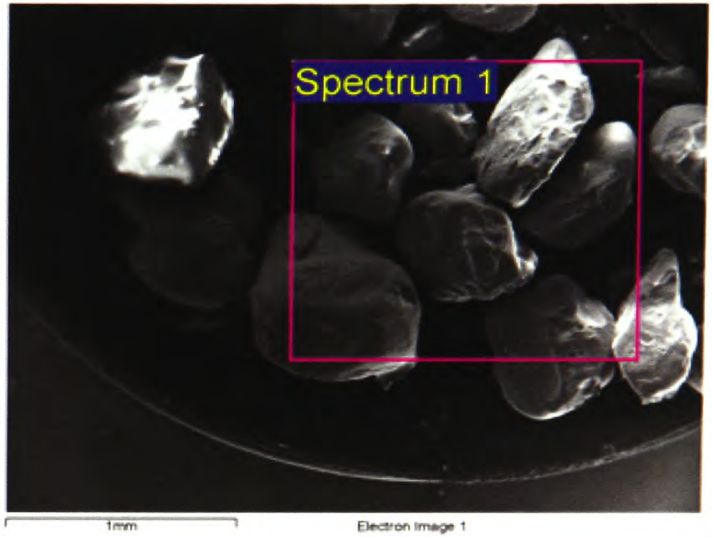
Spectrum processing :
Peaks possibly omitted : 6.402, 7.048 keV

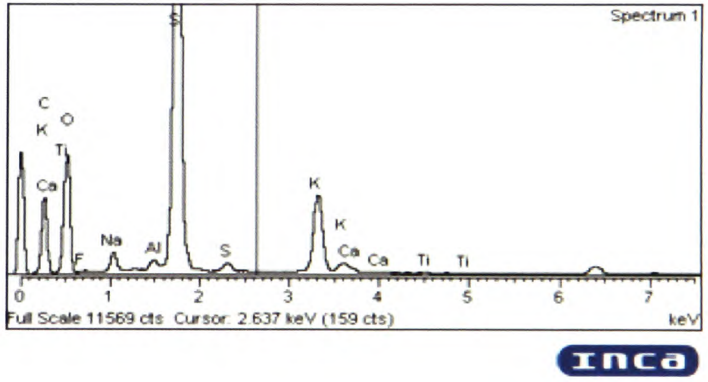
Processing option : All elements analyzed (Normalised)
Number of iterations = 7

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	38.42	49.93
O K	38.44	37.51
F K	0.55	0.46
Na K	1.38	0.93
Al K	0.26	0.15
Si K	16.75	9.31
S K	0.39	0.19
K K	3.57	1.42
Ca K	0.20	0.08
Ti K	0.04	0.01
Totals	100.00	

Comment:
Sample 16 110210





E15: SEM results of Natural gas-Raffinate Sample 1

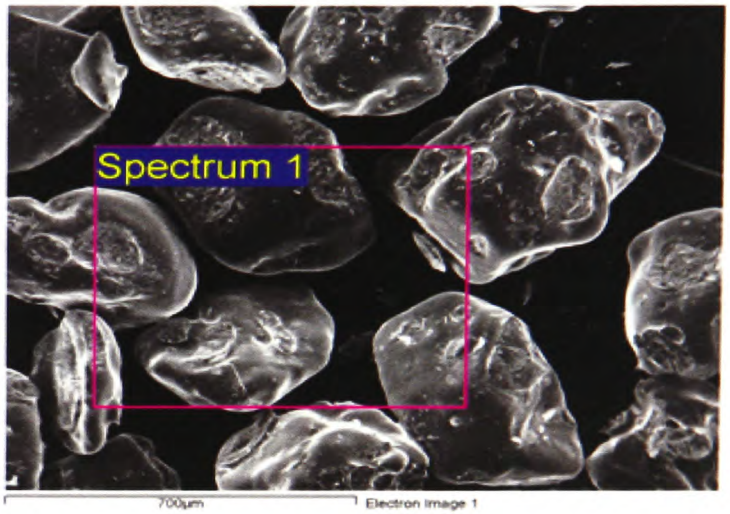
Spectrum processing :
No peaks omitted

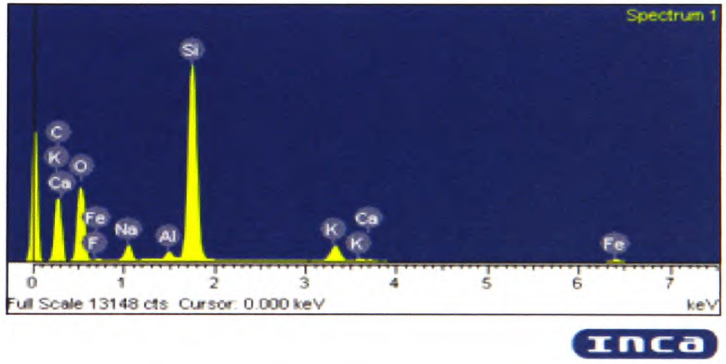
Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	51.44	65.84
F K	-0.08	-0.09
Na K	4.48	3.99
Al K	1.23	0.94
Si K	35.32	25.75
K K	4.60	2.41
Ca K	0.42	0.21
Fe K	2.59	0.95
Totals	100.00	

Comment:
Sample 21, Site of interest 1





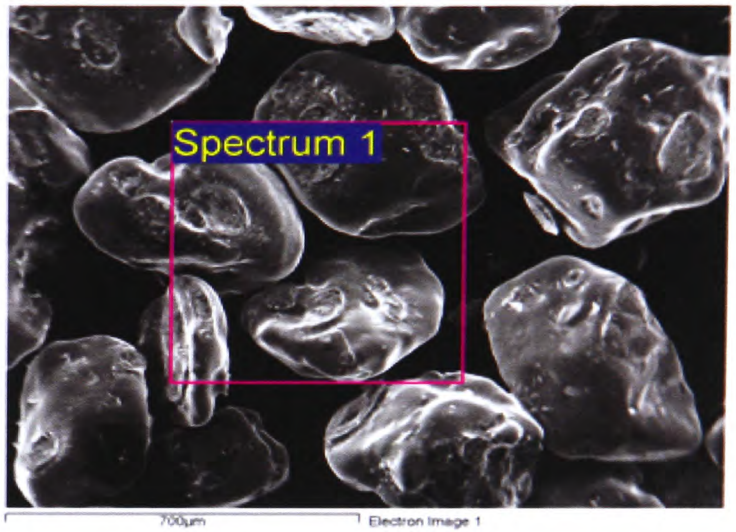
E16: SEM results of Natural gas-Raffinate Sample 2

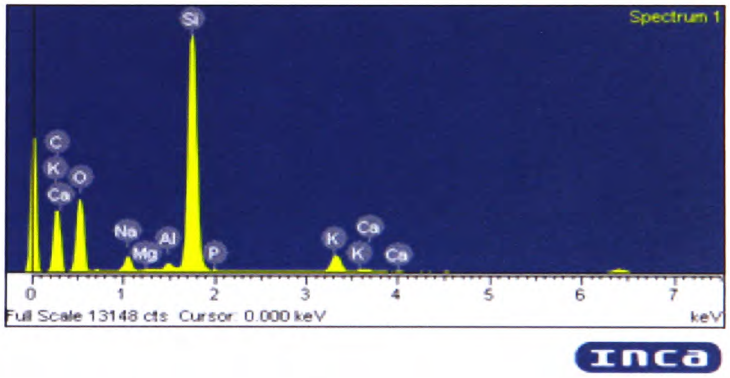
Spectrum processing :
Peaks possibly omitted : 0.706, 6.405, 7.048 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
O SiO2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	50.22	64.20
Na K	3.70	3.29
Mg K	0.19	0.16
Al K	0.85	0.64
Si K	39.57	28.81
P K	0.23	0.15
K K	4.86	2.54
Ca K	0.38	0.19
Totals	100.00	





Comment:
Sample 21 Site of interest 2

E17: SEM results of Coal-Vinasse Sample 1

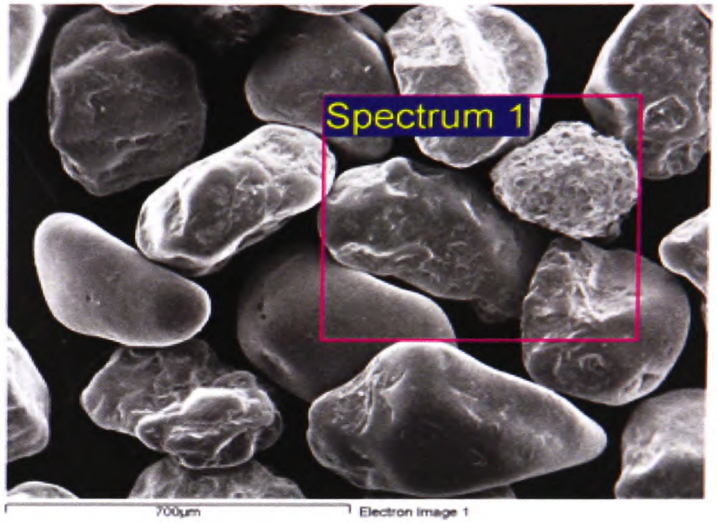
Spectrum processing :
Peaks possibly omitted : 6.400, 7.056 keV

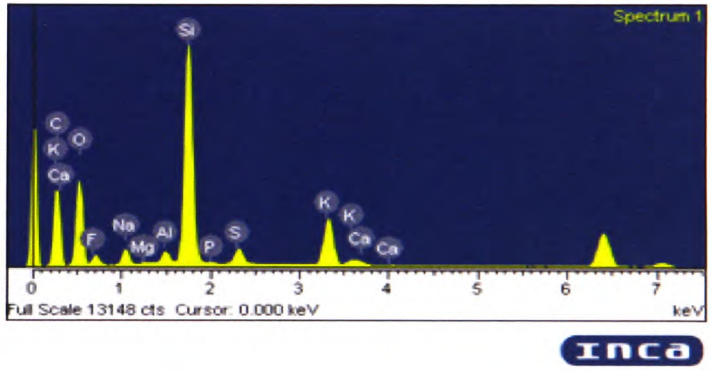
Processing option : All elements analyzed (Normalised)
Number of iterations = 5

Standard :
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	48.29	62.23
F K	4.64	5.03
Na K	3.46	3.10
Mg K	0.30	0.26
Al K	1.35	1.03
Si K	28.37	20.83
P K	0.26	0.18
S K	2.85	1.83
K K	9.84	5.19
Ca K	0.63	0.32
Totals	100.00	

Comment:
Sample 22 Site of interest 1





E18: SEM results of Coal-Vinasse Sample 2

Spectrum processing :
Peak possibly omitted : 4.505 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	40.98	60.40
F K	-1.76	-2.18
Na K	3.37	3.46
Mg K	0.40	0.39
Al K	2.13	1.86
Si K	23.48	19.71
P K	0.23	0.17
S K	3.33	2.45
K K	10.22	6.16
Ca K	0.82	0.48
Fe K	16.80	7.09
Totals	100.00	

Comment:
Sample 22 Site of interest 2